Electronic Supporting Information for:

Synthetic Investigations of Low-Coordinate (*N*-Phosphinoamidinate) Nickel Chemistry: Agostic Alkyl Complexes and Benzene Insertion into Ni-H

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Experimental Section

General Considerations. Unless stated, all experiments were conducted at ambient temperature under nitrogen in an inert-atmosphere glovebox or by using standard Schlenk techniques using oven-dried glassware. Dry, oxygen-free solvents were used unless otherwise indicated. Benzene, toluene, and pentane were deoxygenated and dried by sparging with nitrogen and subsequent passage through a double-column solvent purification system packed with alumina and copper-Q5 reactant. Tetrahydrofuran and diethyl ether were purified by distillation under nitrogen from Na/benzophenone. Deuterated solvents, cyclooctene, $SiMe_4$ and Me_2PhSiH were degassed via three freeze–pump–thaw cycles. All purified/degassed chemicals were stored over 4 Å molecular sieves. **[(PN)NiCl]$_2$**,[1] **[(PN)NiH]$_2$**,[2] **(PN)NiO*t*Bu**,[3] and **(PN)NiNHdipp**[3] were synthesized according to literature procedures. All other reagents were purchased from commercial suppliers and used without further purification. Unless otherwise stated, ^{1}H, ^{13}C, and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.7, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ for ^{1}H and ^{13}C, and 85% H_3PO_4 in D_2O for ^{31}P. ^{1}H and ^{13}C NMR chemical shift assignments are based on data obtained from ^{13}C-UDEFT, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{1}H–^{15}N HMQC NMR experiments. In some cases, fewer than expected unique ^{13}C NMR resonances were observed, despite prolonged acquisition times. Splitting patterns are abbreviated as follows: br, broad; app, apparent; s, singlet; d, doublet; t, triplet; m, multiplet, with all coupling constants (J) reported in Hertz (Hz). Crystallographic data were obtained at or below 193(2) K on a Bruker D8/APEX II CCD diffractometer equipped with a CCD area detector, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Unit cell parameters were determined and refined on all reflections. Data reduction, correction for Lorentz polarization, and absorption correction were each performed. Structure solution and least-squares refinement on F^2 were used throughout. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full crystallographic solution and refinement details are provided in the deposited CIFs (CCDC 1950518-1950519).

Synthesis of 1. In the glovebox, **(PN)NiNHdipp** (0.079 g, 0.012 mmol) was dissolved in benzene (*ca.* 10 mL) in a glass vial containing a magnetic stirring bar to form a dark brown solution. Stirring was initiated, and Me_2PhSiH (18.4 µL, 0.012 mmol) was added by micropipette. After 48 h, the solution had turned red-brown. Removal of benzene *in vacuo* left a sticky solid. This material was triturated with pentane (*ca.* 1 mL), then extracted with pentane (*ca.* 8 mL), concentrated *in vacuo*, and cooled to -35 °C overnight, whereupon an amorphous solid precipitated. The supernatant was decanted, and the solid was dried *in vacuo*. This solid was washed with cold (-35 °C) $SiMe_4$ (3 x *ca.* 250 µL) and pentane (*ca.* 500 µL). The resultant powder was suspended in cold $SiMe_4$ (*ca.* 4 mL), and the suspension was filtered through Celite. The filter cake was flushed with benzene (*ca.* 4 mL) through the filter into a separate glass vial, then dried *in vacuo*. Finally, this material was washed with cold $SiMe_4$ (3 x *ca.* 500 µL), then dried *in vacuo*, leaving **1** as an analytically pure red powder. Yield: 0.030 g, 48%. Single crystals of **1** suitable for X-ray diffraction were grown from a concentrated solution of pentane at -35 °C. Anal. Calcd for $C_{60}H_{88}N_4Ni_2P_2$: C, 68.98; H, 8.49; N, 5.36. Found: C, 68.57; H, 8.22; N, 5.41. ^1H NMR (500 MHz, benzene-d_6): δ 7.71 – 7.70 (m, 4H, H_{arom}) 7.13 – 7.02 (overlapping resonances, 6H, H_{arom}), 6.93 (overlapping resonances, 6H, H_{arom}), 4.11 (m, 2H, CH_EMe_2), 3.61 (m, 2H, CH_K) 3.28 (m, 2H, CH_J), 3.21 (m, 2H, CH_BMe_2) 2.01 – 1.99 (m, 2H, $CHCHCH_IH$), 1.46 – 1.37 (overlapping resonances, 26 H, $CHCHCHH_{I'}$, $CHMe_FMe_D$, $PCMe_{H3}$), 1.24 (d, 6 H $^3J_{PH}$ = 13 Hz, $PCMe_{G3}$), 1.17 (d, 6 H, $^3J_{HH}$ = 7 Hz, $CHMe_CMe_A$), 1.05 (d, 6 H, $^3J_{HH}$ = 7 Hz, $CHMe_FMe_D$), 0.74 (d, 6 H, $^3J_{HH}$ = 7 Hz, $CHMe_CMe_A$).

$^{13}C\{^1H\}$ NMR (125.8 MHz, benzene-d_6): δ 176.1 (N*C*N), 151.1 (C_{arom}), 142.9 (C_{arom}), 141.9 (C_{arom}), 137.4 (m, C_{arom}), 131.8 (CH_{arom}), 128.7 (CH_{arom}), 127.0 (CH_{arom}) 124.5 (CH_{arom}), 123.8 (CH_{arom}), 123.4 (CH_{arom}), 74.2 (C_KHCHCH$_2$) 46.4 (CHC_JHCH$_2$), 38.4 (m, P*C*Me$_{H3}$) 37.3 (m, P*C*Me$_{G3}$) 29.1 (C_EHMe$_2$) 28.7 (PC*Me*$_{H3}$), 28.4 (overlapping resonances, PC*Me*$_{G3}$ and C_BHMe$_2$), 25.7(CHC_IH$_2$), 25.2 (CH*Me*$_F$Me$_D$), 24.8 (CH*Me*$_C$Me$_A$), 23.8 (CHMe$_F$*Me*$_D$), 23.2 (CHMe$_C$*Me*$_A$). $^{31}P\{^1H\}$ (202.5 MHz, benzene-d_6): δ 111.9 (accompanying minor signals at 114.1 and 110.3 ppm, with each being *ca* 6% of the major signal at 111.9 ppm).

Synthesis of 2. In the glovebox, a glass vial was charged with **[(PN)NiCl]$_2$** (0.66 mg, 0.064 mmol) and then benzene (*ca*. 8 mL), forming a dark purple-red solution. To this solution, EtLi (0.5 M in cyclohexane/benzene, 255 uL, 0.128 mmol) was added as a single aliquot. The dark orange reaction mixture was sealed with a Teflon screw-cap, shaken vigorously, and then immediately filtered through Celite, leaving a dark filter cake and a dark red-orange filtrate. The filtrate was concentrated *in vacuo* to a brown powder, which was extracted with pentane (*ca*. 5 mL) and filtered through Celite, leaving a brown filter cake and a purple filtrate. Removal of pentane *in vacuo* gave a dull purple powder, consisting of **2** alongside a <10 % impurity consisting of the isomeric compound **2’** and trace **3**. 42 mg, 60%. Anal. Calcd for $C_{29}H_{45}N_2NiP$: C, 68.12; H, 8.87; N, 5.48. Found: C, 67.88; H, 8.59; N, 5.37. ^1H NMR (500 MHz, benzene-d_6): δ 7.60 – 7.58 (m, 2 H, H_{arom}), 7.16 (overlapping with C_6D_6, 1 H, H_{arom}) 7.02 (m, 2 H, H_{arom}), 6.95– 6.90 (overlapping resonances, 3 H, H_{arom}), 3.79 (apparent septet, 2 H, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 1.43 (d, 18 H, $^3J_{HP}$ = 14 Hz, P(C*Me*$_3$)$_2$), 1.32 (d, 6 H, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$) 1.07 (d, 6 H, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 0.50 (m, 2 H, NiC*H*$_2$CH$_3$), -1.93 (m, 3H, NiCH$_2$C*H*$_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz, benzene-d_6): δ 175.8 (C_{arom}), 150.4 (C_{arom}), 142.6 (C_{arom}), 137.8 (d, $^3J_{CP}$ = 19 Hz), 130.1 (CH_{arom}), 128.3 (overlapping with solvent, CH_{arom}), 127.1 (CH_{arom}), 125.0 (CH_{arom}), 123.5 (CH_{arom}), 36.9 (d, $^1J_{PC}$ = 30 Hz, P(*C*Me$_3$)$_2$), 28.6 (overlapping resonances, P(C*Me*$_3$)$_2$ and *C*HMe$_2$), 25.2 (CH*Me*$_2$), 22.8 (CH*Me*$_2$), 2.7 (d, $^2J_{CP}$ = 12 Hz, Ni*C*H$_2$CH$_3$), -6.5 (d, $^3J_{CP}$ = 3 Hz, NiCH$_2$*C*H$_3$). ^{31}P{^{1}H} (202.5 MHz, benzene-*d*$_6$): δ 128.7.

Synthesis of 3. In the glovebox, a glass vial was charged with a magnetic stirring bar, **[(PN)NiCl]$_2$** (0.058 g, 0.056 mmol), and pentane (*ca*. 4 mL). Magnetic stirring was initiated to afford a dark red-purple slurry, which was then was cooled to -35 °C. In a separate glass vial, *n*-BuLi (1.6 M in hexanes, 70 μL, 0.112 mmol) was diluted with pentane (*ca*. 2 mL), and cooled to -35 °C in the glovebox freezer. Each vial was removed from the freezer, magnetic stirring was re-initiated, and the solution containing *n*-BuLi was immediately added dropwise (*ca*. 3 drops /sec) to the slurry containing **[(PN)NiCl]$_2$**. The color of the slurry turned from dark red-purple to orange over the course of the addition. Immediately afterwards, the vial was cooled to -35 °C. After *ca*. 60 min, the vial contained a red-orange supernatant and dark precipitate, and the contents were filtered through Celite, giving a cloudy yellow filtrate and a dark filter cake (soluble in C_6H_6; consisting of **[(PN)NiCl]$_2$**, **3**, and multiple unidentified phosphorus- and/or hydride-containing products). This filtrate was cooled to -35 °C. After *ca*. 4 h, additional precipitate had formed, so the filtrate was filtered again, yielding a clear orange eluent, and a yellow-orange filter cake. This filtrate was cooled at -35 °C overnight, then filtered once more. ^{31}P{^{1}H} NMR analysis of this pentane filtrate indicated confirmed the presence of **3** in acceptably high purity. Removal of pentane *in vacuo* yielded **3** as an orange solid. Yield: 0.02 g, 30%. Anal. Calcd for $C_{31}H_{49}N_2NiP$: C, 69.03; H, 9.16; N, 5.19. Found: C, 69.32; H, 8.87; N, 5.12. ^{1}H NMR (300 MHz, benzene-*d*$_6$): δ 7.66 – 7.63 (m, 2 H, H_{arom}), δ 7.02 (overlapping resonances, 3 H, H_{arom}), 6.96 – 6.90 (overlapping resonances, 3 H, H_{arom}), 3.80 (apparent septet, 2 H, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 1.46 (d, 18 H, $^3J_{HP}$ = 14 Hz, P(C*Me*$_3$)$_2$, 1.35 (d, 6 H, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 1.11 – 1.03 (overlapping resonances, 8 H, CH*Me*$_2$ and NiCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.58 – 0.49 (overlapping resonances, 5 H, NiC*H*$_2$CH$_2$CH$_2$CH$_3$ and

$NiCH_2CH_2CH_2CH_3$), -2.50 (m, 2H, $NiCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 175.4 (N*C*N), 151.4 (C_{arom}), 142.4 (C_{arom}), 137.6 (d, $^3J_{CP}$ = 19 Hz), 130.3 (CH_{arom}), 128.3 (overlapping with solvent, CH_{arom}), 127.1 (CH_{arom}), 124.7 (CH_{arom}), 123.5 (CH_{arom}), 36.9 (d, 1 J_{PC} = 30 Hz, $P(CMe_3)_2$), 28.6 (overlapping resonances, $P(CMe_3)_2$ and $CHMe_2$), 25.1 ($CHMe_2$), 24.8 ($CH_{2\gamma}$), 14.8 ($CH_{3\delta}$), 14.6 (d, $^3J_{CP}$ = 2 Hz, $CH_{2\beta}$), 9.8 (d, $^2J_{CP}$ = 12 Hz, $CH_{2\alpha}$). $^{31}P\{^1H\}$ (121.5 MHz, benzene-d_6): δ 128.3.

Generation of 4. In the glovebox, a glass vial was charged with a magnetic stirring bar, **[(PN)NiCl]$_2$** (0.054 g, 0.052 mmol), and pentane (*ca*. 6 mL). Magnetic stirring was initiated, and the resultant slurry was cooled to -35 °C. In a separate glass vial, *n*-hexyllithium (2.3 M in hexanes, 46.5 μL, 0.107 mmol, 2.05 equiv) was added to cold (-35 °C) pentane (*ca*. 4 mL), and re-cooled to -35 °C in the glovebox freezer. These vials were removed from the freezer, magnetic stirring was re-initiated, and the solution containing *n*-hexyllithium was immediately added dropwise (*ca*. 3 drops / sec) to the slurry containing **[(PN)NiCl]$_2$**. The color of the slurry turned from dark red-purple to orange over the course of the addition, and immediately afterwards, the vial was cooled to -35 °C. After 90 min, the vial was cloudy orange, and the contents were filtered through Celite, giving a cloudy orange filtrate and a dark filter cake. This filtrate was cooled to -35 °C. After *ca*. 12 h, the filtrate was filtered again, yielding a clear orange filtrate and a dark and yellow filter cake. The filtrate was sampled for NMR, indicating presence of retained **[(PN)NiCl]$_2$**. Solvent was removed in vacuo, and resultant orange solid was brought up in cold $SiMe_4$ (*ca*. 2 mL) and filtered through Celite. Removal of solvent *in vacuo* yielded an oily dark solid which was characterized as a mixture of **4** (possibly including internal isomers) and **[(PN)NiCl]$_2$** in a *ca*. 7 : 1 : 1 ratio. While **4** is not claimed herein as an isolated analytically pure compound, the formation of **4** from *n*-hexyllithium in this manner provides independent support for the identity of this complex in reactions that involve **2** and **3** as described in the text. ^{1}H NMR (300 MHz, benzene-d_6): δ 7.67 – 7.64 (m, 2 H, H_{arom}), 7.07 – 6.92 (overlapping resonances, 6 H, H_{arom}), 3.80 (apparent septet, 2 H, $^{3}J_{HH}$ = 7 Hz, C*H*Me$_2$), 1.47 (d, 18 H, $^{3}J_{HP}$ = 14 Hz, P(C*Me*$_3$)$_2$, 1.35 (d, 6 H, $^{3}J_{HH}$ = 7 Hz, CH*Me*$_2$), 1.16 – 0.57 (overlapping resonances, 17 H, CH*Me*$_2$, Ni*n*Hex), -2.45 (m, 2H, Ni*n*Hex$_{\beta}$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6): δ 175.4 (N*C*N), 151.1 (d, $^{3}J_{CP}$ = 3 Hz, C_{arom}), 142.3 (C_{arom}), 137.6 (d, $^{3}J_{CP}$ = 19 Hz C_{arom}), 130.3 (CH$_{arom}$), 128.3 (overlapping with solvent, CH$_{arom}$), 127.1 (CH$_{arom}$), 124.7 (CH$_{arom}$), 123.6 (CH$_{arom}$), 36.9 (d, $^{1}J_{PC}$ = 30 Hz, P(*C*Me$_3$)$_2$), 32.8 (CH$_{2\delta}$), 31.4 (CH$_{2\gamma}$), 28.7 – 28.6 (overlapping resonances, P(C*Me*$_3$)$_2$ and *C*HMe$_2$), 25.1 (CH*Me*$_2$), 23.0 (CH*Me*$_2$), 22.4, (CH$_{2\varepsilon}$), 14.1 (CH$_{3\zeta}$), 12.8, (d, $^{3}J_{CP}$ = 2 Hz, CH$_{2\beta}$), 10.2 (d, $^{2}J_{CP}$ = 12 Hz, CH$_{2\alpha}$). ^{31}P{^{1}H} (121.5 MHz, benzene-d_6): 128.5.

Synthesis of 5. In the glovebox, a glass vial was charged with **[(PN)NiCl]$_2$** (100 mg, 0.097 mmol) and benzene (*ca*. 6 mL). This purple-red solution was frozen at -35 °C. In a separate vial, neopentyllithium (0.017 mg, 0.19 mmol) was dissolved in benzene (*ca*. 2.5 mL), and frozen at -35 °C. These vials were removed from the freezer, and immediately upon the thawing of each, the solution containing neopentyllithium was added dropwise (*ca*. 2 drops /sec) to the solution containing **[(PN)NiCl]$_2$**. The solution was allowed to stand at ambient temperature for 17 h, at which point the reaction mixture had turned brown. Following removal of benzene *in vacuo*, the resultant solid was triturated with pentane (4 x *ca.* 1 mL), extracted into pentane (*ca*. 8 mL) and filtered through Celite, leaving a dark filter cake and a red-brown filtrate. Removal of pentane *in vacuo* yielded a red-brown semicrystalline solid. Yield: 0.098 g, 93%. Crystals of **5** suitable for single-crystal X-ray diffraction were grown from a concentrated solution of pentane at -35 °C. Anal. Calcd C, 69.43; H, 9.29; N, 5.06. Found: C, 69.56; H, 9.15; N, 4.70. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.57 – 7.53 (m, 2 H, H_{arom}), 7.07 – 6.98 (overlapping resonances, 3 H, H_{arom}), 6.91

– 6.87 (overlapping resonances, 3 H, H_{arom}), 4.06 (apparent sept, 2 H, C*H*Me_2), 1.58 – 1.53 (overlapping resonances, 24 H, CHMe_2 and P*tBu*), 0.98 (d, 6 H, $^3J_{HH}$ = 7 Hz, CHMe_2), 0.76 (d, J = 2 Hz, 9 H, $CH_2C$$Me_3$), 0.12 (d, 2 H, $^3J_{HP}$ = 3 Hz, C$H_2$$CMe_3$). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): δ 171.1 (N*C*N), 145.6 (C_{arom}), 143.5 (C_{arom}), 137.0 (d, $^3J_{CP}$ = 20 Hz, C_{arom}), 130.6 (CH_{arom}), 128.5 (CH_{arom}), 127.2 (CH_{arom}), 125.2 (CH_{arom}), 123.8 (CH_{arom}), 38.3 (d, $^1J_{CP}$ = 30 Hz, P(*C*Me_3)$_2$), 32.1 (d, $^3J_{CP}$ = 2 Hz, CH_2*C*Me_3), 29.2 ($CH_2C$$Me_3$), 28.8 – 28.7 (overlapping resonances, P(CMe_3)$_2$ + *C*HMe_2), 24.9 (CHMe_2), 23.3 (CHMe_2), 9.9 (d, $^2J_{CP}$ = 26 Hz, *C*$H_2$$CMe_3$). $^{31}P\{^1H\}$ (202.5 MHz, benzene-d_6): 113.4.

Procedure for determining concentration effects of benzene in the formation of 1. (PN)NiO*t*Bu (0.030 g, 0.054 mmol) was dissolved in benzene (750 μL). This dark green solution was split into three 250 μL portions (A, B, C) in three glass vials. Portion A was diluted with benzene (500 μL), B with benzene and cyclohexane (250 μL each), and C with cyclohexane (500 μL). Then 250 μL of a solution of Me_2PhSiH in cyclohexane (composed of 15 μL and 1359 μL, respectively; 0.018 mmol) was added to each, and samples A – C were transferred to NMR tubes. Conversion of **(PN)NiO*t*Bu** and yields of **1** and **[(PN)NiH]$_2$** were determined by use of ^{31}P qNMR methods.[4]

General procedure for reactions involving ethylene or H_2. In the glovebox, a J-Young tube was charged with solvent (500 – 750 uL), metal complex (0.005 – 0.010 g), and sealed. The tube was cycled onto an evacuated Schlenk line equipped with a mercury bubbler, which was then pressurized with the desired gas (~ 1 atm). After the headspace of the tube was exposed to vacuum (*ca*. 5 sec), the contents of the tube were exposed to the gas, and the reaction was monitored by use of NMR methods. In some cases, where a higher concentration of dissolved gas was desired, the contents of the tube were degassed via three freeze-pump-thaw cycles.

Computational Details. Geometries were optimized using UM06-L/6-31G(d,p)[LANL2DZ] with the Gaussian 09 program (revision B.01; Gaussian, Inc.: Wallingford, CT, 2009).[5]

Tabulated NMR Data and Supporting NMR Spectra

	2	**3**	**4**	**5**
$^{1}J_{CH}$ α-CH_2 (Hz)	150.5	149.5	146.8	128.3
$^{1}J_{CH}$ β- or γ-agostic (Hz)	122.5 (β)	117.1 (β)	116.0 (β)	122.5 (γ)

Table S1. Summary of average $^{1}J_{CH}$ coupling constants for complexes **2** – **5** (300 K).

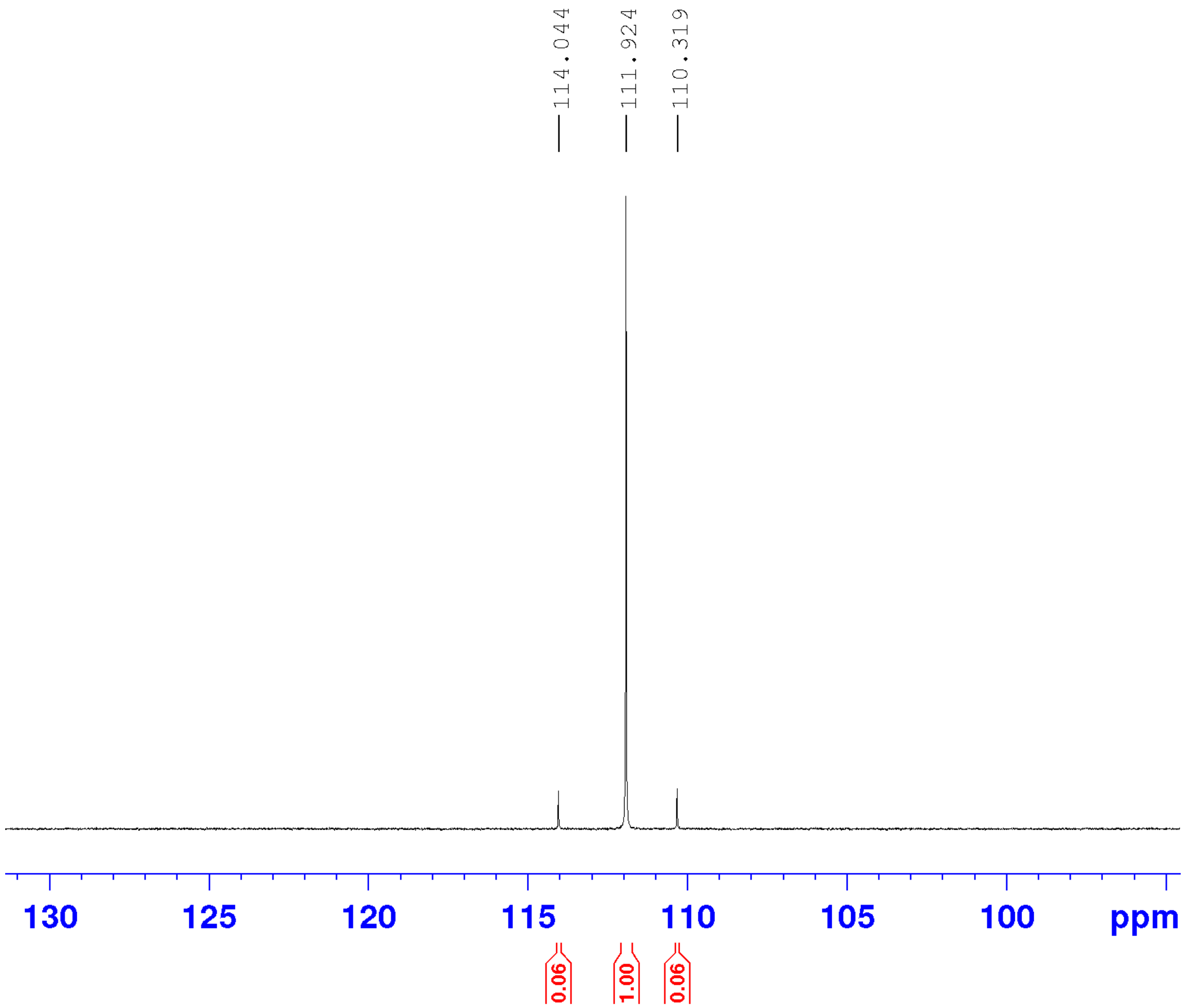

Figure S1. $^{31}P\{^1H\}$ NMR spectrum of of **1** (202.5 MHz, benzene-d_6).

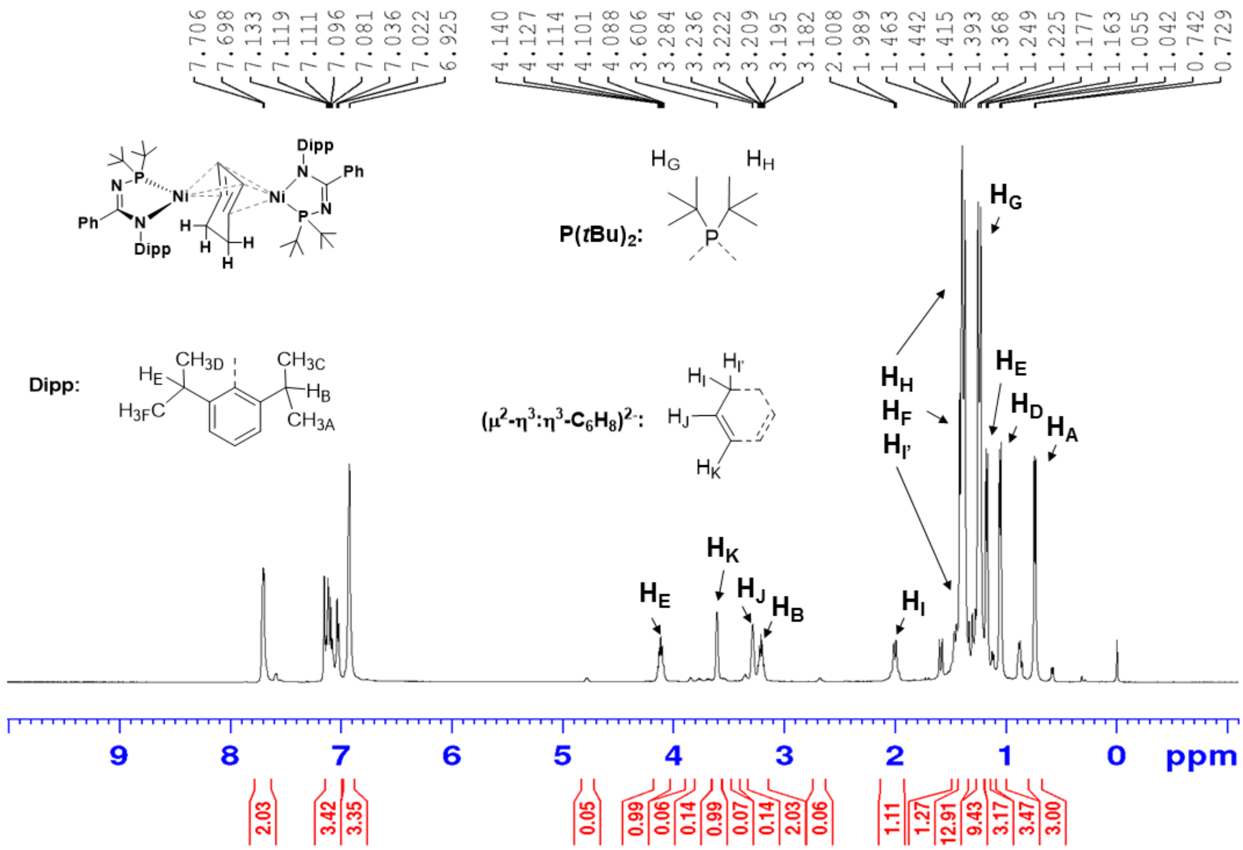

Figure S2. ^{1}H NMR spectrum of **1.** *Integrations correspond to the asymmetric unit of* **1**. (500 MHz, benzene-d_6).

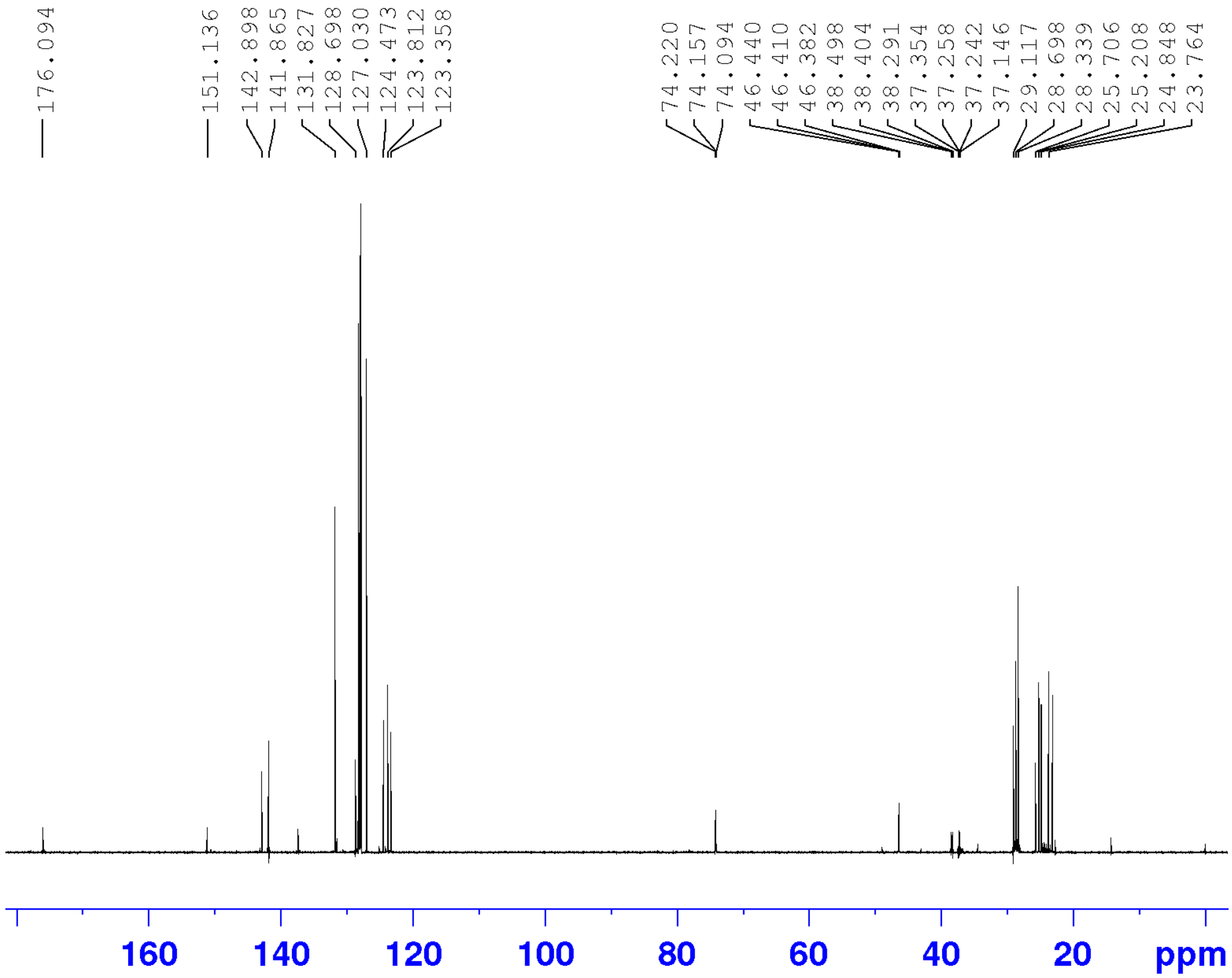

Figure S3. $^{13}C\{^{1}H\}$ UDEFT spectrum of **1** (125.7 MHz, benzene-d_6).

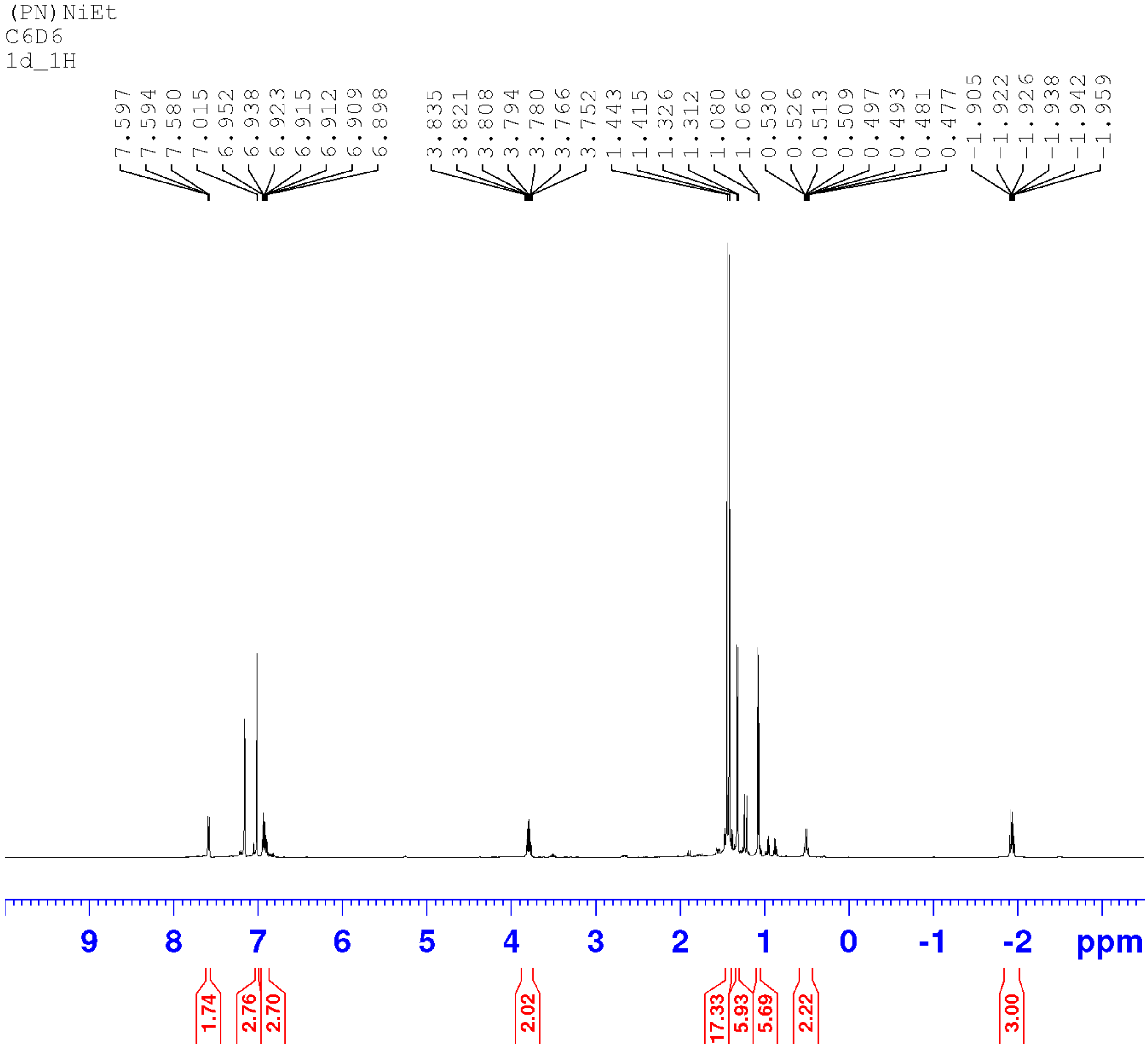

Figure S4. ^{1}H NMR spectrum of **2** (500 MHz, benzene-d_6).

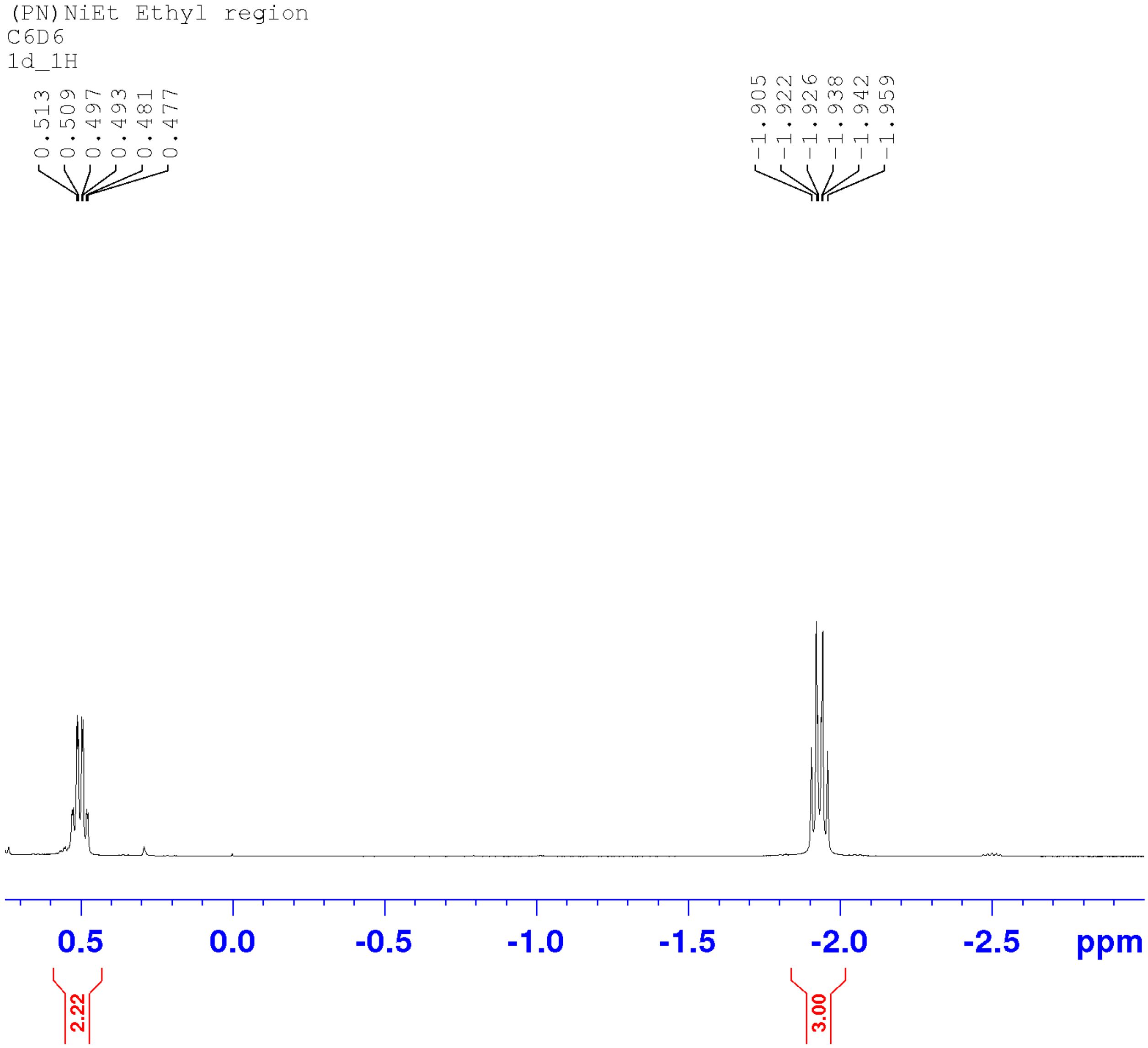

Figure S5. Low-frequency region of the ^{1}H NMR spectrum of **2** (500 MHz, benzene-d_6).

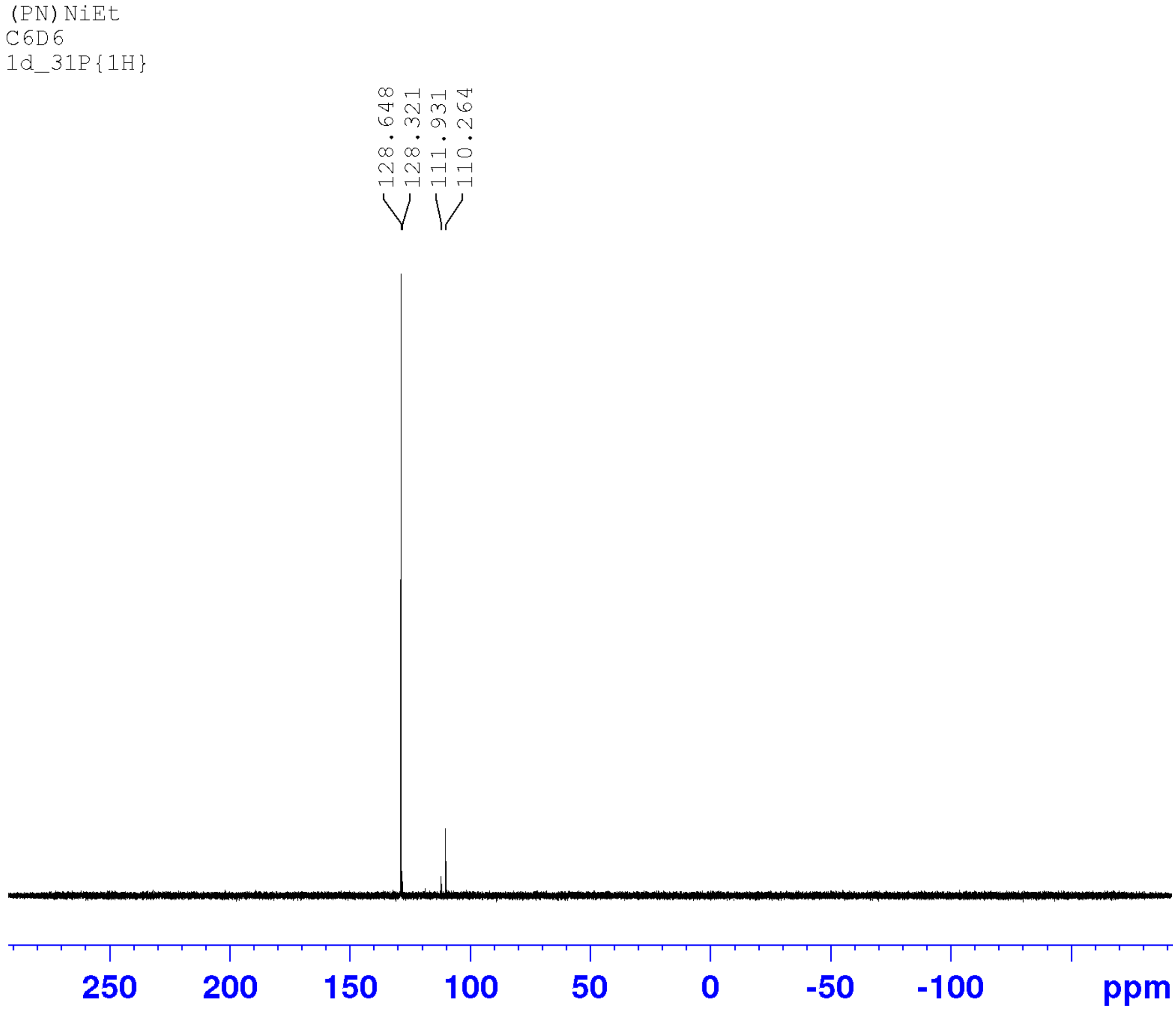

Figure S6. $^{31}P\{^1H\}$ NMR spectrum of **2** (202.5 MHz, benzene-d_6).

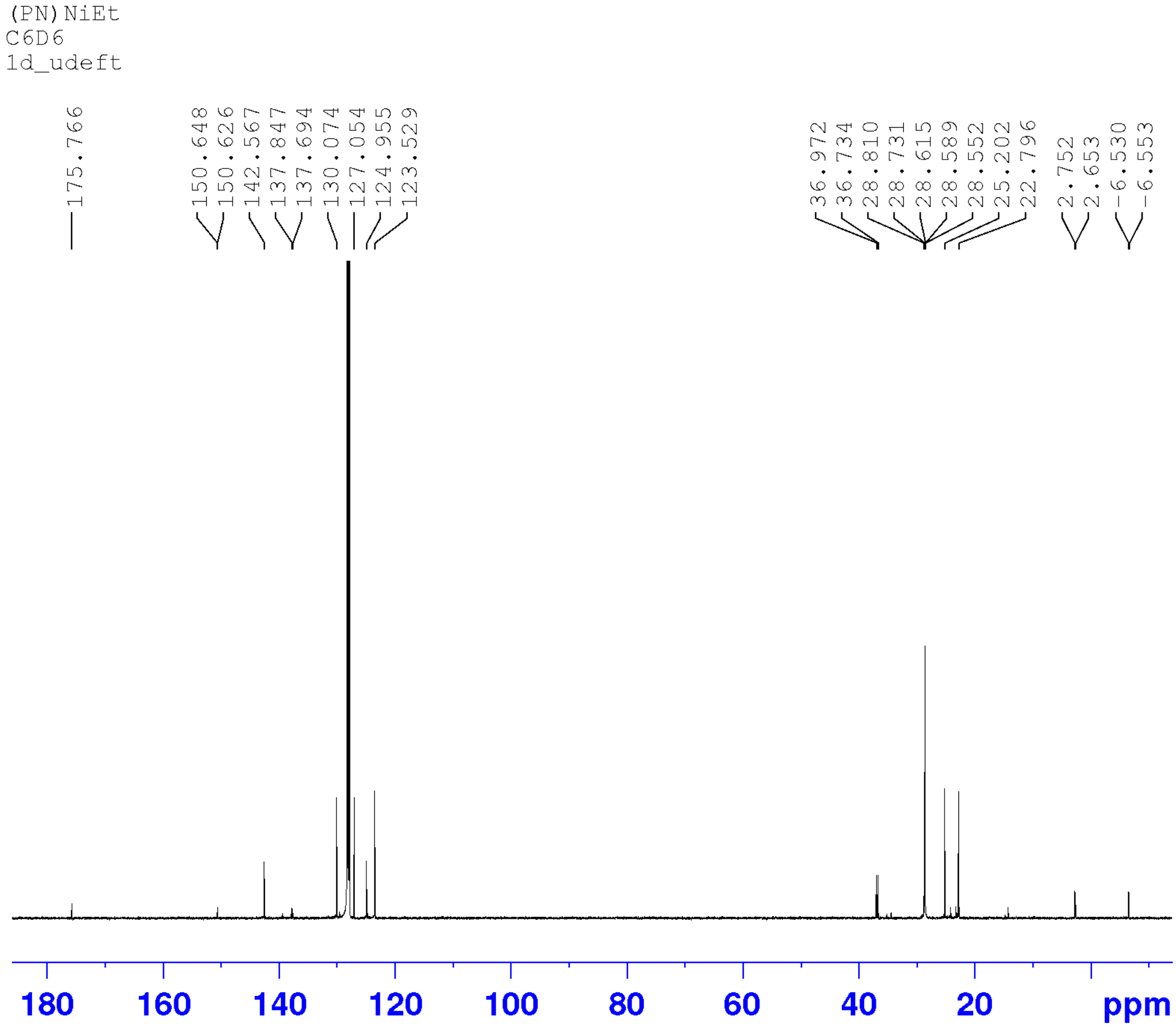

Figure S7. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum of **2** (75.5 MHz, benzene-d_6).

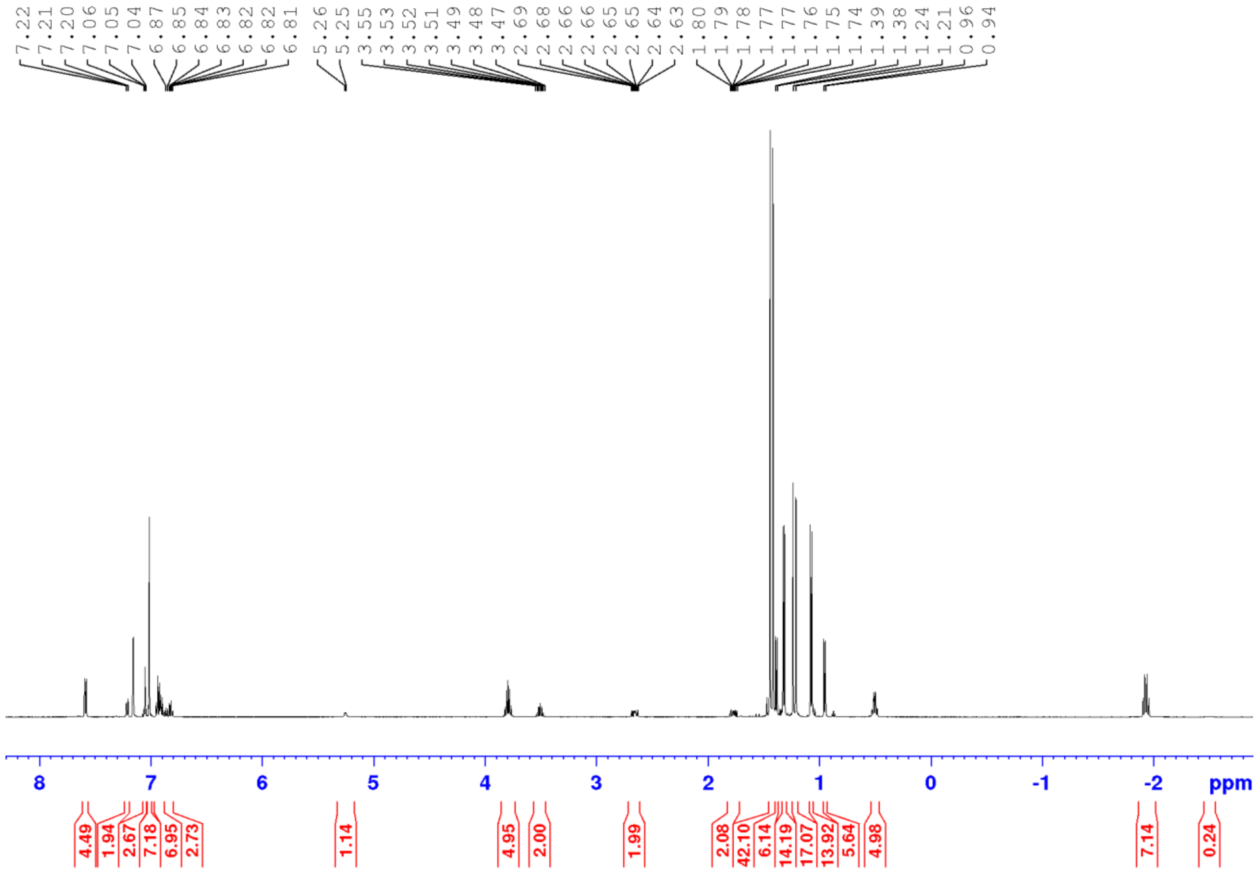

Figure S8. ^{1}H NMR spectrum of a mixture of **2**, **2’**, and **3** (500 MHz, benzene-d_6).

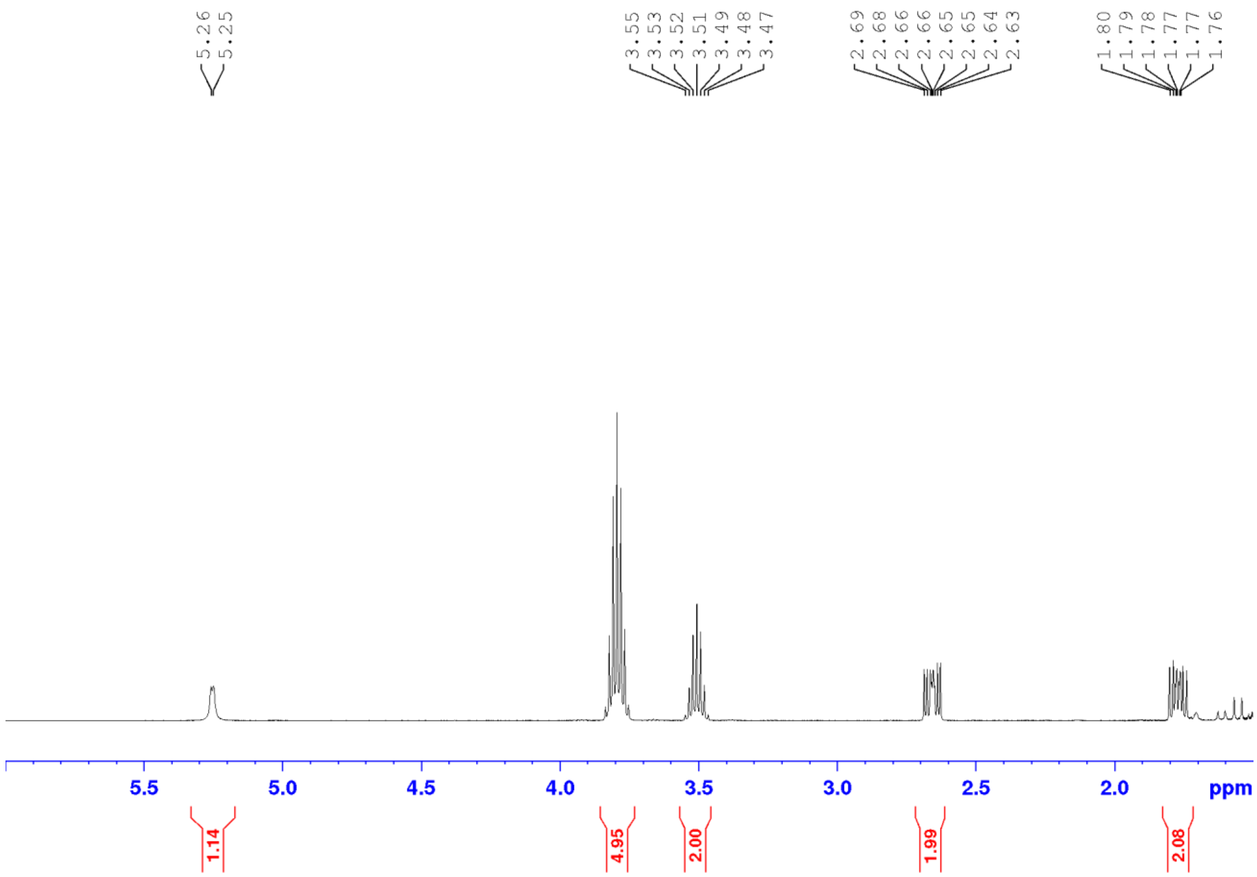

Figure S9. Region of the [1]H NMR spectrum of a mixture of **2**, **2'**, and **3** featuring the tentatively assigned NH and ethylene resonances of **2'** (500 MHz, benzene-d_6).

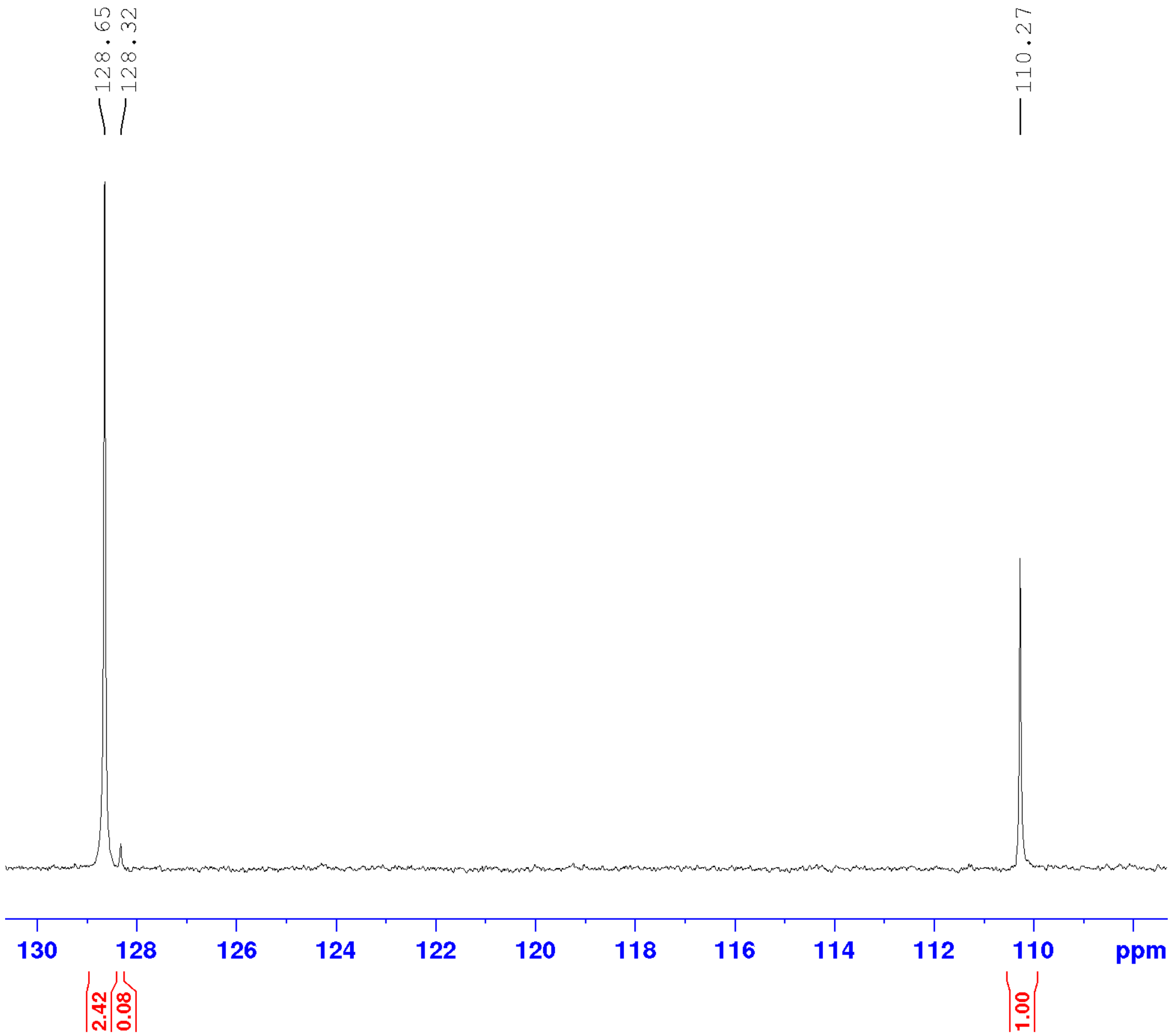

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of **2**, **2’**, and **3** (202.5 MHz, benzene-d_6).

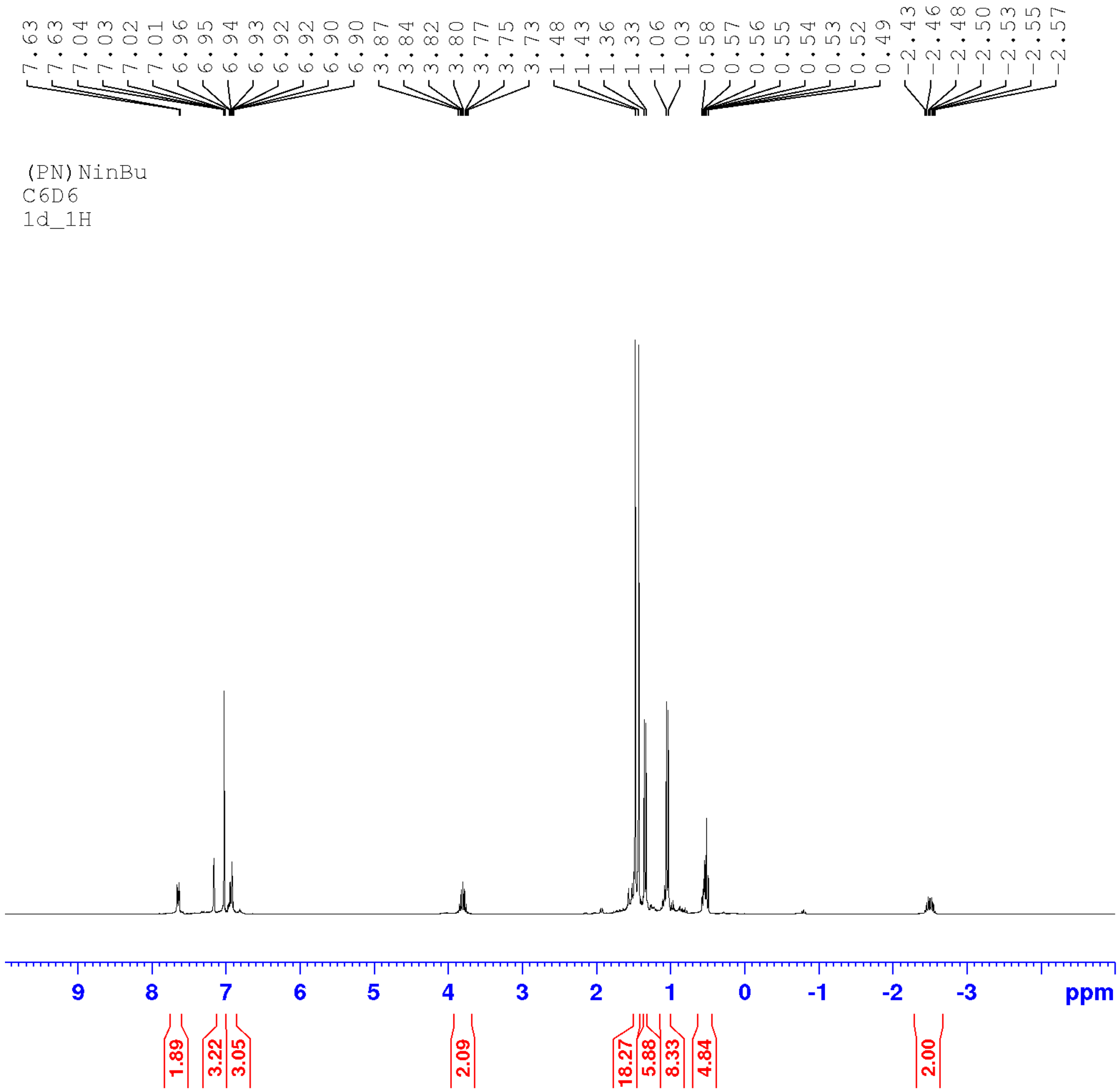

Figure S11. ^{1}H NMR spectrum of **3** (300 MHz, benzene-d_6).

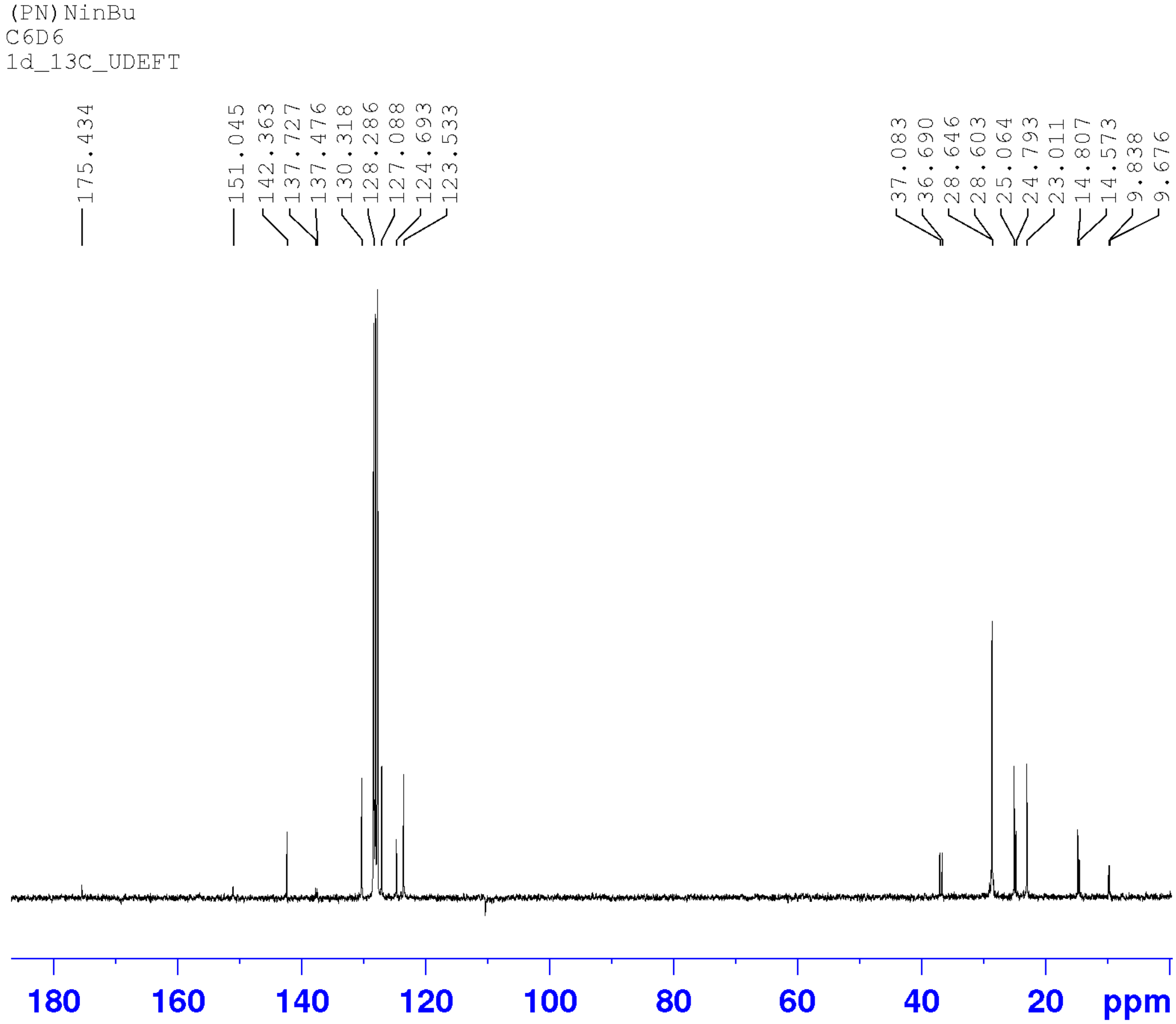

Figure S12. $^{13}C\{^{1}H\}$ UDEFT spectrum of **3** (75.5 MHz, benzene-d_6).

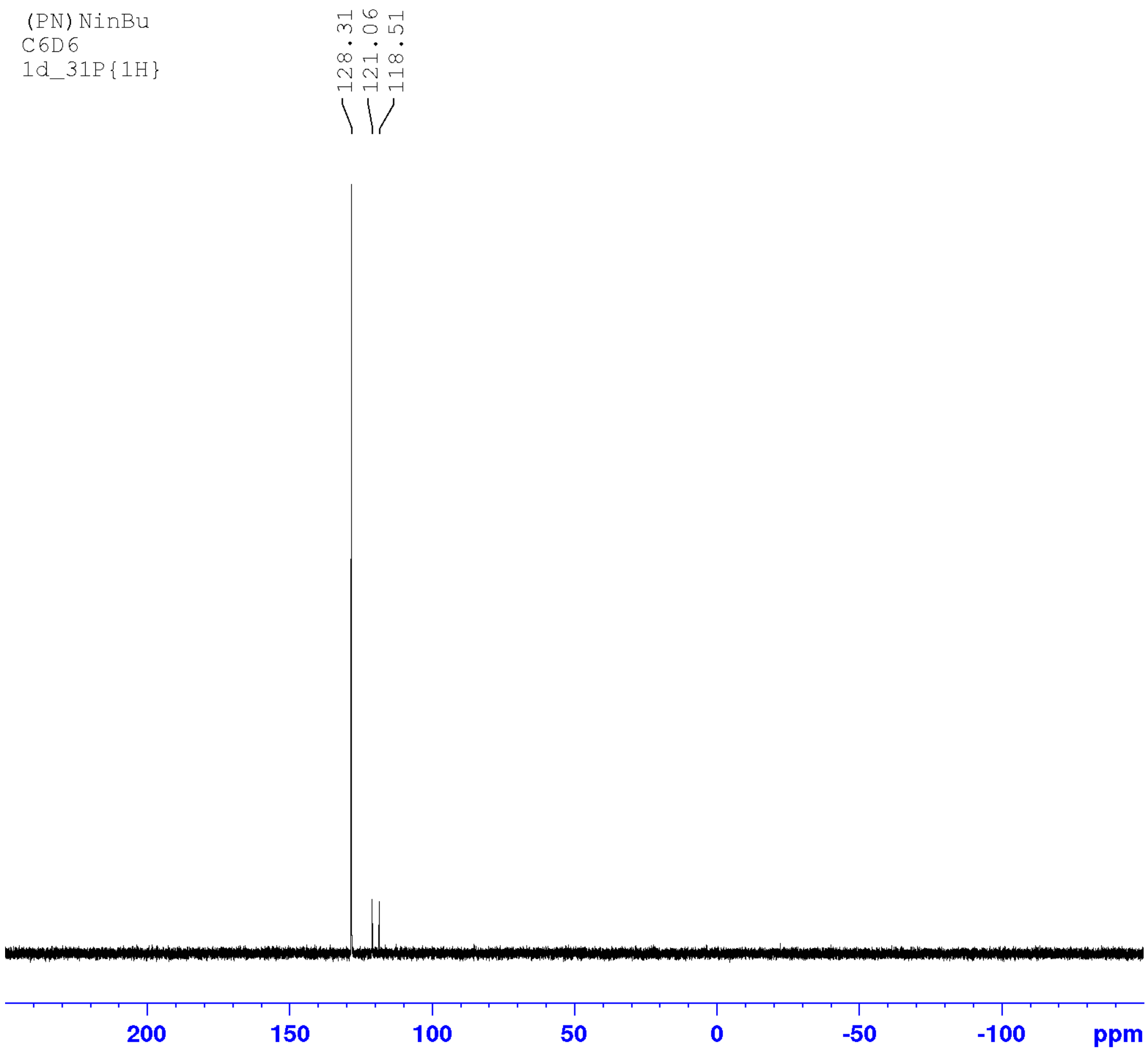

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **3**. (121.5 MHz, benzene-d_6)

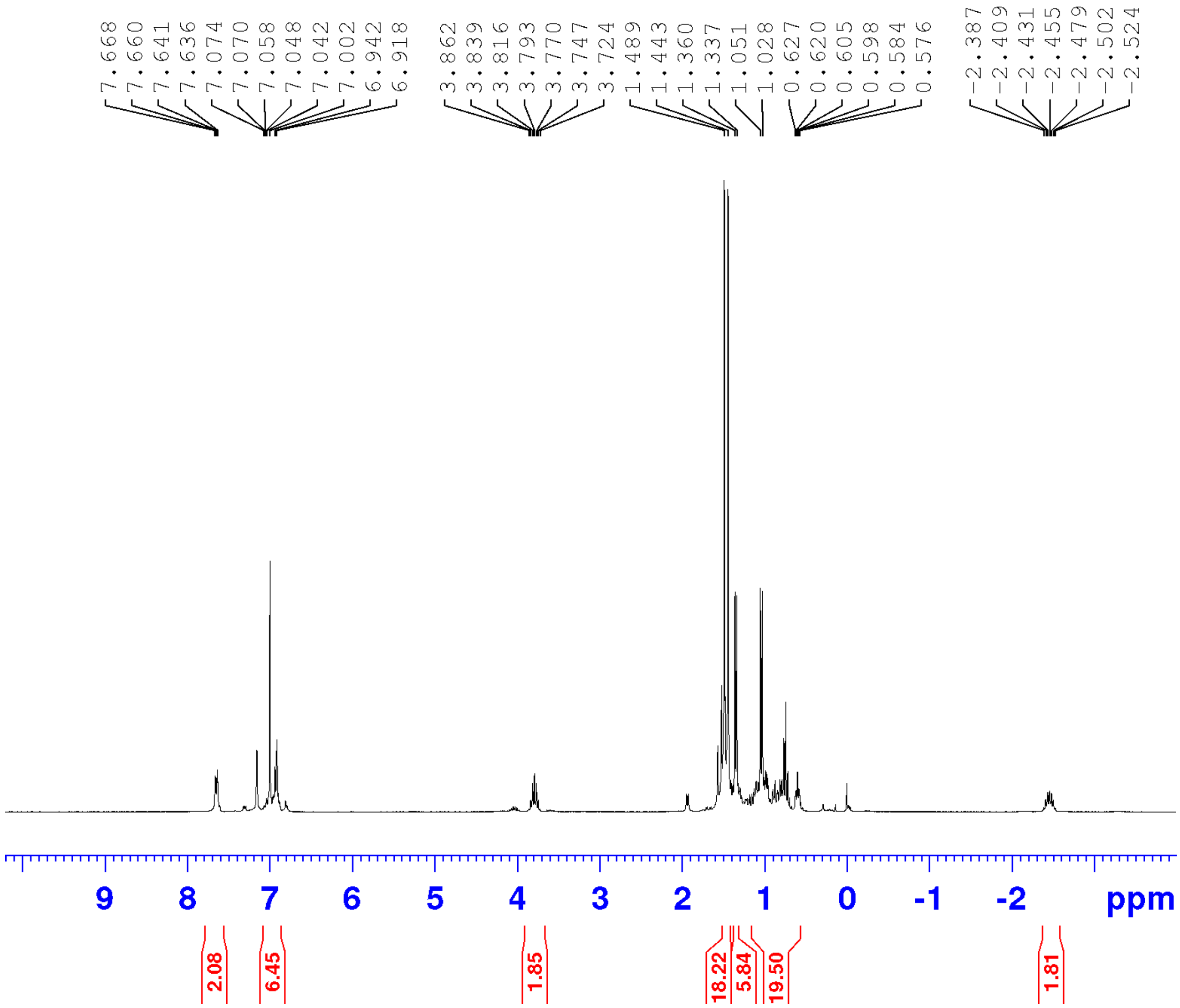

Figure S14. ^{1}H NMR spectrum of **4** (300 MHz, benzene-d_6).

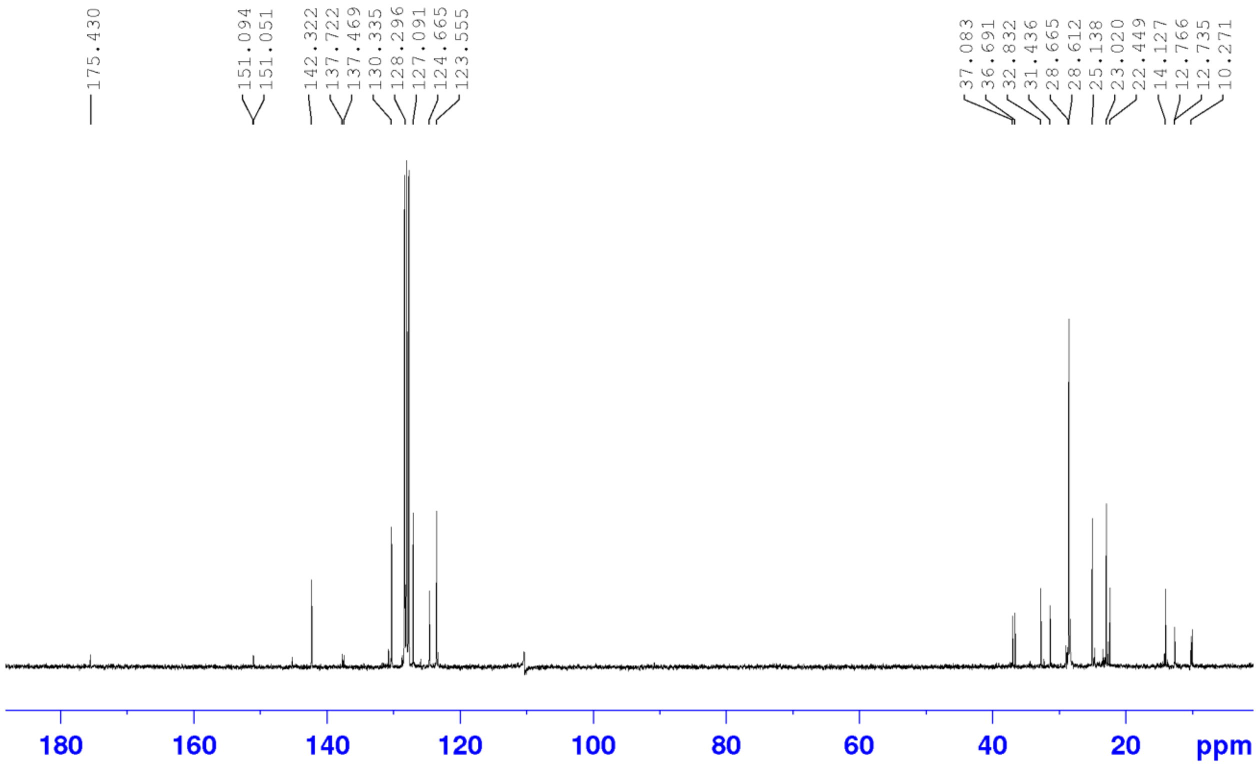

Figure S15. $^{13}C\{^1H\}$ UDEFT NMR spectrum of **4** (75.5 MHz, benzene-d_6).

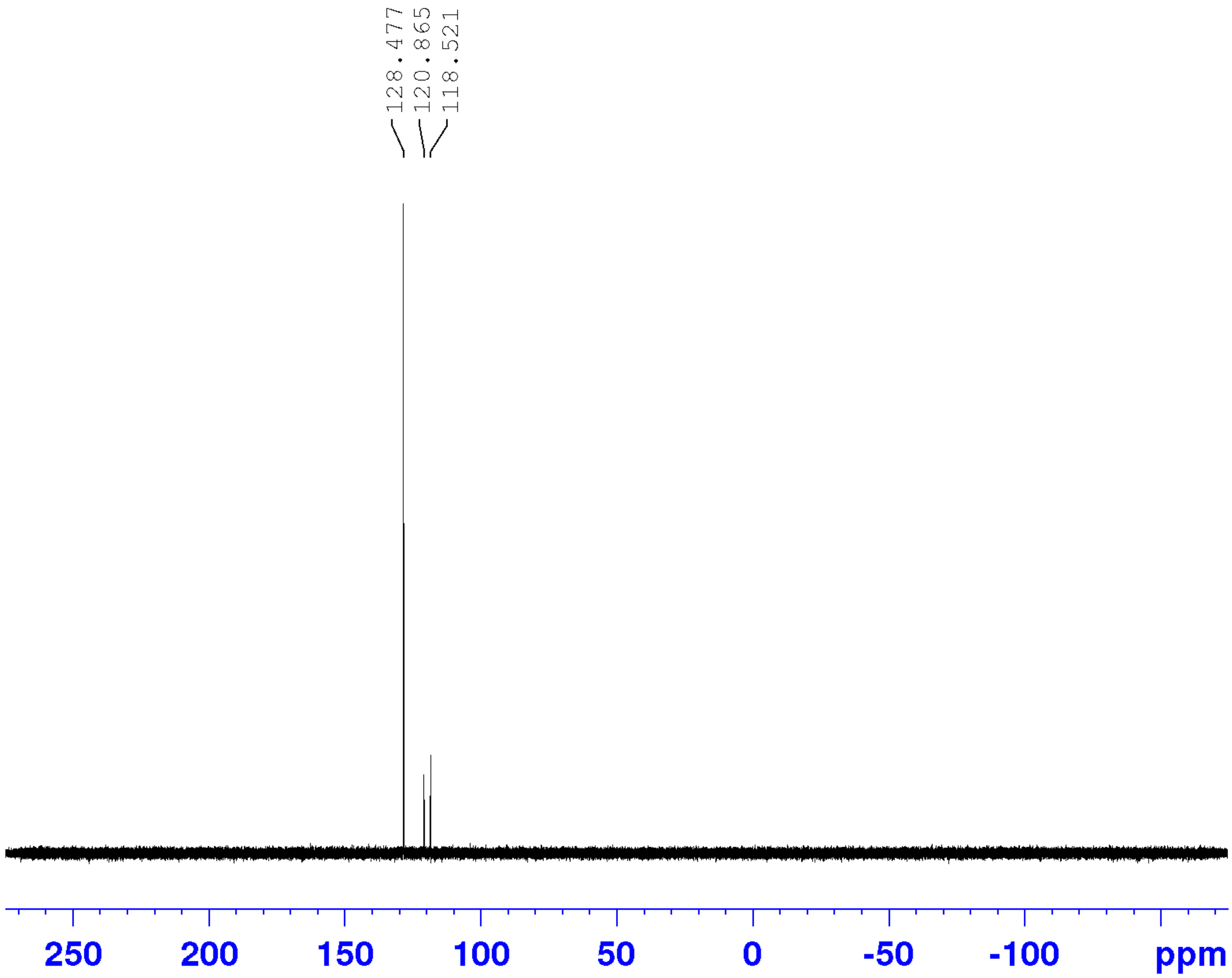

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **4** (121.5 MHz, benzene-d_6).

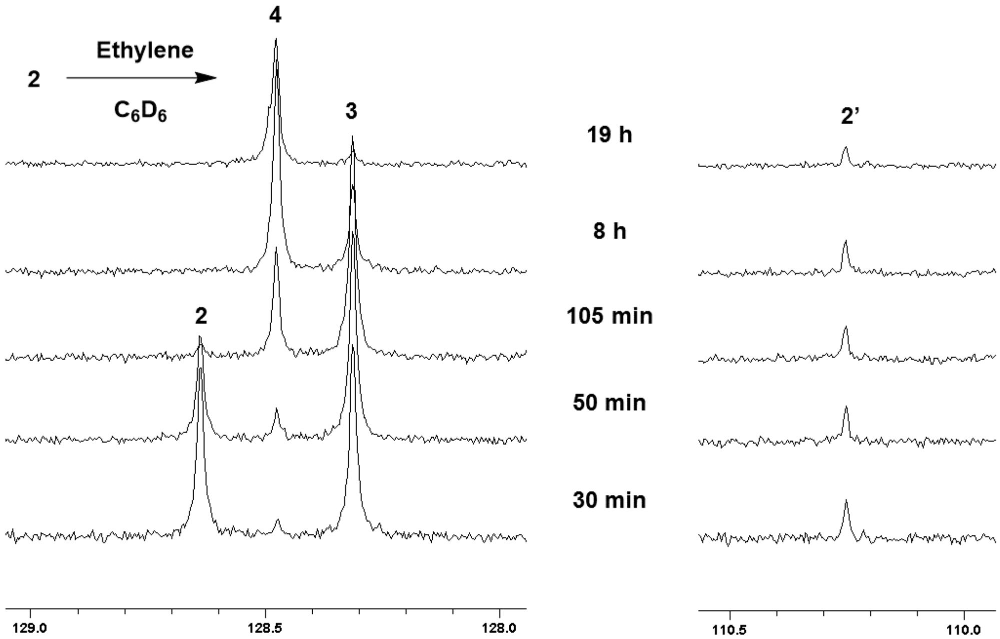

Figure S17. Stacked $^{31}P\{^1H\}$ NMR spectra of the reaction of **2** with ethylene (121.5 MHz, benzene-d_6; shifts in ppm).

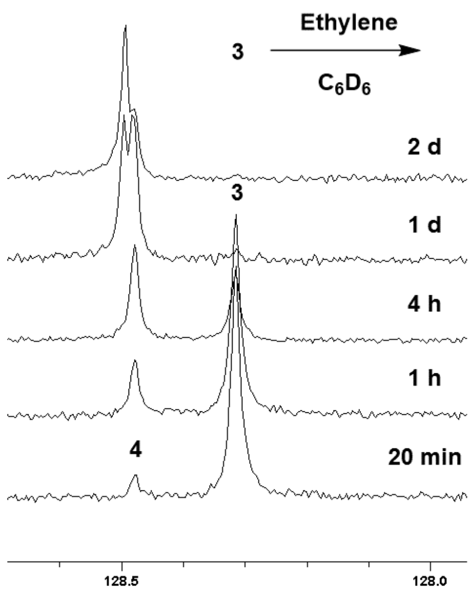

Figure S18. Stacked $^{31}P\{^1H\}$ NMR spectra of the reaction of **3** with ethylene (121.5 MHz, benzene-d_6; shifts in ppm).

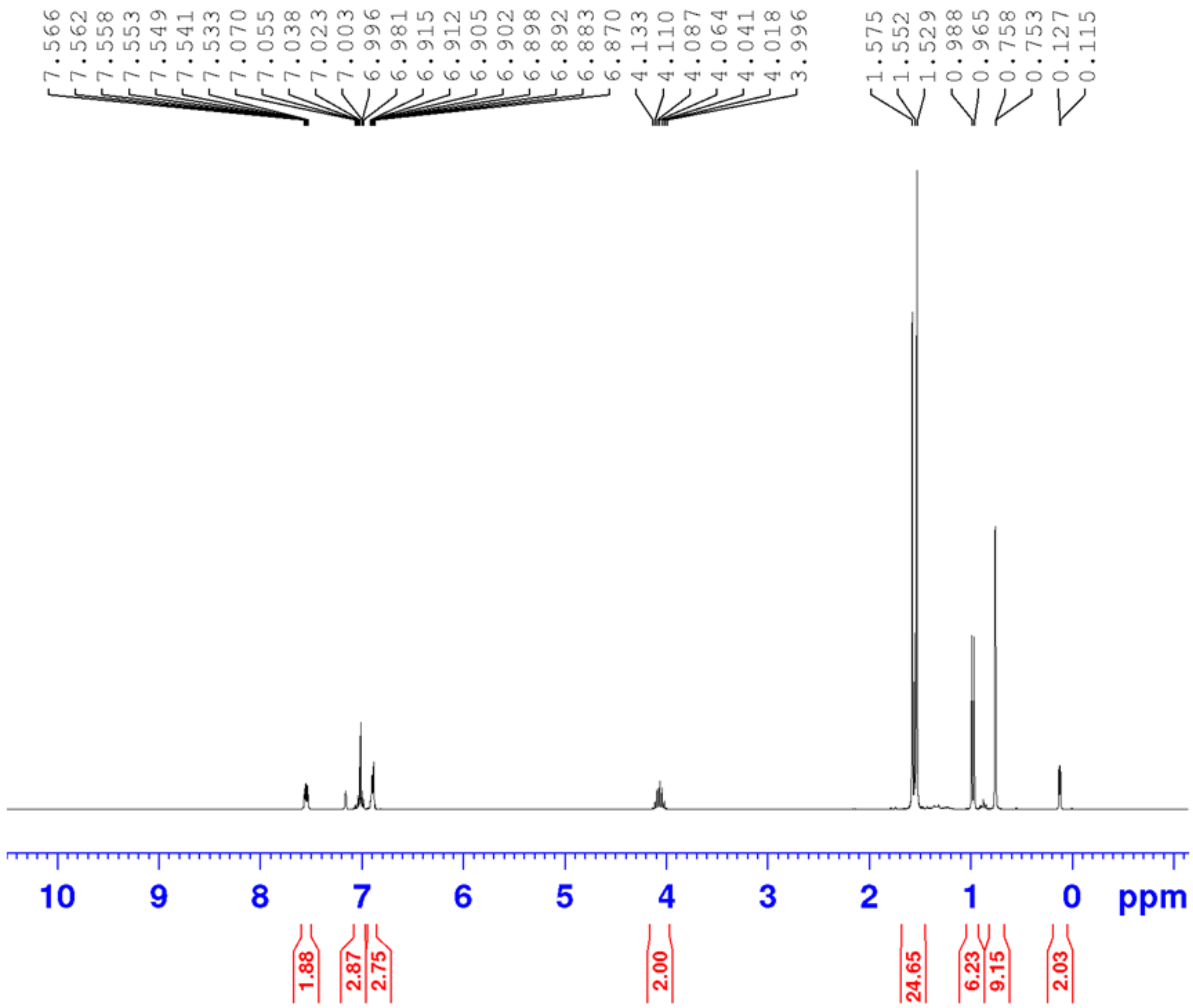

Figure S19. ^{1}H NMR spectrum of **5** (300 MHz, benzene-d_6).

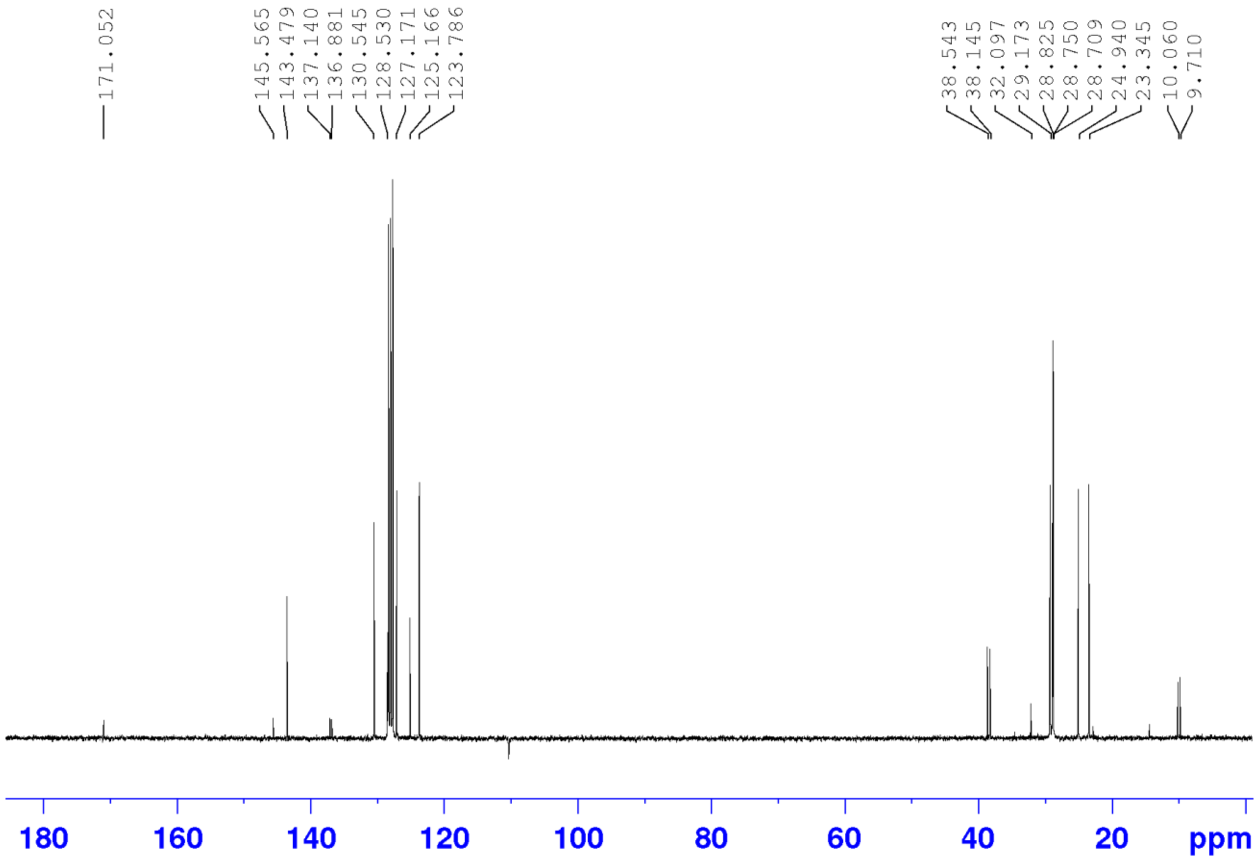

Figure S20. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum of **5** (75.5 MHz, benzene-d_6).

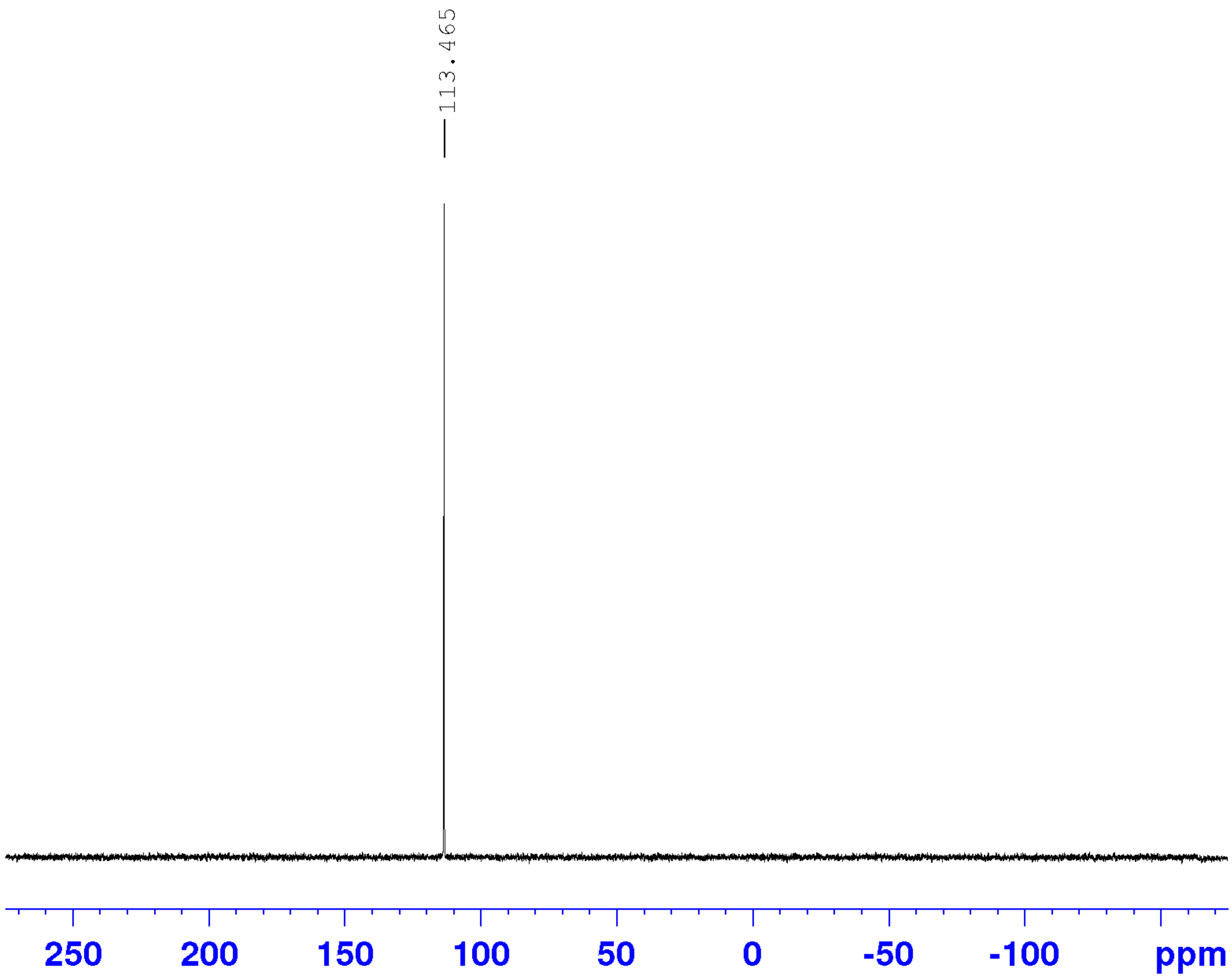

Figure S21. $^{31}P\{^1H\}$ NMR spectrum of **5** (121.5 MHz, benzene-d_6).

Supporting Computational Information

The **(PN)NiH**, **[(PN)NiH]$_2$** and **[(PN)Ni]$_2$C$_6$H$_8$** (**1**) geometries were optimized with the M06-L/6-31G**[LANL2DZ for Ni] with an ultrafine integration grid using Gaussian 09 program. Vibrational frequencies were calculated to verify stationary point which resulted in all positive frequencies. M06L functional was chosen because it provides an accurate estimate of relative spin-state energies and reaction energies for first-row transition metal complexes. Reported free energies at 298K and 1 atm for **(PN)NiH**, **[(PN)NiH]$_2$** and **[(PN)Ni]$_2$C$_6$H$_8$** correspond to M06-L/def2-TZVP//M06-L/6-31G**[LANL2DZ for Ni]. The def2-TZVP basis set was obtained from Basis Set Exchange Portal (https://www.basissetexchange.org). The Kohn-Sham molecular orbitals shown in Figure 1 and Figure 2 in the manuscript were generated using GaussView 6.0 with an isovalue of 0.03.

M06-L xyz coordinates (Å) and energies (Hartrees)

(PN)NiH
(M06-L/6-31G**[LANL2DZ for Ni])
Electronic Energy = -1673.709711
Electronic and Zero-Point Energy = -1673.086438
Enthalpy = -1673.051044
Free Energy = -1673.148724
M06-L/def2-TZVP
Electronic Energy = -3013.055056

P	-0.03779000	2.14154800	-0.06949400
N	1.21701600	-0.26642600	-0.39885800
C	-0.29648100	2.76323000	1.68031800
N	1.61952500	2.04909600	-0.29993700
C	0.55463800	1.83705800	2.55490000
H	0.38170500	2.06812000	3.61258600
H	1.62249100	1.95753000	2.34685100
H	0.29543500	0.78416100	2.39129500
C	-1.76216100	2.62349400	2.08887200
H	-1.87388300	2.90750000	3.14233000
H	-2.10810600	1.59240600	1.97027900
H	-2.42591800	3.26485300	1.50318400
C	0.18125600	4.20396000	1.85007500
H	-0.46959700	4.91644900	1.33331300
H	1.20345900	4.33648400	1.48102800
H	0.17077900	4.46852100	2.91448500
C	-0.61269000	3.33586000	-1.39151400
C	0.34568400	4.52104600	-1.52700000
H	0.06884800	5.10341700	-2.41401500
H	1.37783100	4.18151600	-1.64141200
H	0.30118200	5.19528200	-0.66821600
C	-2.03753000	3.81584600	-1.13664000

H	-2.09639300	4.48964900	-0.27538900
H	-2.72298400	2.97766300	-0.96977100
H	-2.39609500	4.37476100	-2.00923100
C	-0.57203100	2.51699800	-2.68774200
H	-0.84382800	3.15649400	-3.53614700
H	-1.27650500	1.67812600	-2.64672800
H	0.43081600	2.11688000	-2.87385200
C	2.05325400	0.79843700	-0.41347400
C	3.52240000	0.65292900	-0.60721700
C	4.37632000	1.57446800	0.01226200
H	3.93256700	2.35594800	0.62303500
C	5.75341800	1.48611100	-0.14914200
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C	6.29910000	0.48583000	-0.95164000
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C	5.45749100	-0.41945500	-1.59386900
H	5.87467800	-1.19194200	-2.23368300
C	4.07912300	-0.34157400	-1.42029200
H	3.43174400	-1.05138800	-1.92697700
C	1.64891200	-1.60219200	-0.24794100
C	2.46541800	-2.03233400	0.82263700
C	2.83811000	-3.37865600	0.87574800
H	3.47288700	-3.71100100	1.69538500
C	2.41104900	-4.29765200	-0.07177800
H	2.72443200	-5.33594900	-0.01025800
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H	1.19314000	-4.60228000	-1.81542000
C	1.15694400	-2.55104900	-1.18134900
C	2.88748400	-1.12546100	1.96174900
H	2.60550700	-0.09717200	1.71671600
C	4.39552900	-1.14958600	2.20049000
H	4.68039600	-0.40752300	2.95385400
H	4.95391600	-0.93323000	1.28483600
H	4.72408300	-2.12792500	2.56937900
C	2.12977500	-1.50166400	3.23595900
H	1.04615200	-1.47180800	3.08052600
H	2.37374600	-0.81547400	4.05481500
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H	-0.40735600	-3.96929000	-3.14130600
H	0.96645700	-3.17132000	-3.91840500
H	-0.67449200	-2.55394200	-4.15410400
C	-1.20509100	-1.85354100	-1.54786600
H	-1.79935300	-2.77450600	-1.52422000

H	-1.81226000	-1.09472800	-2.05577800
H	-1.12558500	-1.62562300	-0.45627900
Ni	-0.69919200	0.17620000	-0.40369200
H	-2.08337500	0.72991800	-0.37348500

[(PN)NiH]$_2$
(M06-L/6-31G**[LANL2DZ for Ni])
Electronic Energy = -3347.498217
Electronic and Zero-Point Energy = -3346.250168
Enthalpy = -3346.178317
Free Energy = -3346.351509
M06-L/def2-TZVP
Electronic Energy = -6026.182276

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N	-4.11889800	4.03581000	0.01144300
C	-3.45951000	1.05115800	-0.19584900
H	-3.61236800	-0.00077200	-0.46723000
H	-4.38826900	1.42917100	0.24337700
H	-2.67391800	1.09090200	0.57076300
C	-1.78111500	1.21300100	-2.01051400
H	-1.99553100	0.18102900	-2.31658800
H	-0.98718300	1.18597000	-1.25449100
H	-1.39314400	1.73929300	-2.88818000
C	-4.18282800	1.80456600	-2.46810600
H	-3.88586800	2.24555900	-3.42520500
H	-5.07438700	2.32723800	-2.10661600
H	-4.45941200	0.76125800	-2.66472300
C	-2.61962700	4.86227600	-2.20377000
C	-1.64010100	4.42881400	-3.28787700
H	-1.48091400	5.25361700	-3.99297800
H	-2.00717700	3.57375300	-3.86505300
H	-0.66424400	4.16657100	-2.86316500
C	-2.08641000	6.13069700	-1.52757900
H	-1.06283600	5.99212200	-1.16236000
H	-2.71303700	6.42977300	-0.68012100
H	-2.07948900	6.95595400	-2.24969400
C	-3.99671600	5.16301000	-2.79804900
H	-3.91213900	6.02206300	-3.47485600
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C	-3.89962700	4.12628900	1.31612300
C	-5.11124700	4.32607400	2.16245400

C	-6.29438600	3.69775000	1.74544700
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C	-7.47199200	4.55007100	3.66842100
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H	-6.31372000	5.79901500	4.98569400
C	-5.13789100	5.08355300	3.34064000
H	-4.24574300	5.59605000	3.68176300
C	-2.37039100	4.03292000	3.22963600
C	-2.76005100	2.94952500	4.05006900
C	-2.44625300	2.98598000	5.40927800
H	-2.73729800	2.14813100	6.03983500
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H	-1.55333700	4.08763500	7.02864500
C	-1.39774400	5.12764400	5.14973400
H	-0.86537400	5.97568400	5.57739500
C	-1.66185200	5.13109100	3.77941900
C	-3.48645500	1.74537700	3.49384800
H	-3.79148900	1.97271600	2.46849000
C	-4.75225800	1.41530700	4.28022200
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H	-4.52298600	1.08315900	5.29912700
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H	-0.67530200	6.97407300	3.70849400
C	-0.22794000	6.03840800	1.86161700
H	-0.73797800	5.57969500	1.00541700
H	0.56478800	5.35715900	2.18716400
H	0.24337900	6.95954500	1.49702100
C	-2.38002400	7.18476100	2.45765600
H	-2.98871500	6.62006800	1.74442700
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N	2.17535000	1.27927200	1.67091100
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C	3.30030400	4.71035900	0.92192300

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H	4.19518000	4.20377800	1.29534500
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H	2.12169800	6.32644500	-0.92993500
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H	4.16251400	4.69358400	-2.43790300
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H	4.63949800	5.78186300	-1.13450900
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C	4.14512200	1.75150700	-2.87033700
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H	4.81142300	1.29734700	-2.13231700
H	4.55108000	2.72795900	-3.14432500
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H	2.20018000	3.59244600	-3.54296500
H	0.80117300	2.71095900	-2.89111700
H	1.72476200	2.04349200	-4.24445700
C	2.17545700	0.41794500	-2.14327900
H	2.18206300	-0.11335000	-3.10274200
H	1.14735700	0.42048300	-1.76060700
H	2.79681200	-0.14552200	-1.44028500
C	3.47918300	1.25503800	1.30940100
C	4.52960000	0.62804000	2.16540600
C	5.76895400	1.28185800	2.23454700
H	5.90654100	2.18495400	1.64715000
C	6.79387600	0.78846800	3.03156700
H	7.74085100	1.31897300	3.08075800
C	6.60992800	-0.38564300	3.75849400
H	7.41120100	-0.77702300	4.37931400
C	5.39445700	-1.05857100	3.67755100
H	5.24499900	-1.98344100	4.22756300
C	4.35801300	-0.55525000	2.89627800
H	3.42104300	-1.09975200	2.85125700
C	1.63822900	0.62168100	2.79944700
C	1.86169300	1.11650800	4.10128700
C	1.33281600	0.40140600	5.17666300
H	1.49920400	0.76150600	6.18913000
C	0.59957900	-0.76291300	4.97626600
H	0.20459100	-1.30966100	5.82867400
C	0.34531700	-1.21276400	3.68394400
H	-0.26411300	-2.10119400	3.53552000
C	0.83837300	-0.52402500	2.57695900
C	2.59649000	2.42264400	4.31332300

H	3.26978000	2.57410000	3.46195200
C	3.45341100	2.44397800	5.57236400
H	4.03808100	3.36801100	5.61865800
H	4.15187300	1.60097900	5.59766900
H	2.84660900	2.40567200	6.48401900
C	1.58053300	3.56509400	4.30086900
H	0.96943400	3.53503600	3.38949300
H	2.07322000	4.54417400	4.35779600
H	0.89139300	3.48370000	5.14884100
C	0.56938800	-0.99668100	1.16155800
H	0.49590500	-0.09102300	0.53372900
C	1.73840200	-1.82657400	0.63014200
H	1.88328600	-2.72416800	1.24379600
H	2.67688700	-1.26291800	0.63778300
H	1.55264800	-2.15327600	-0.39916200
C	-0.73693300	-1.76334500	1.00501100
H	-0.70008500	-2.74379300	1.49381700
H	-0.94088600	-1.94348100	-0.05613400
H	-1.58435300	-1.21166600	1.42278600
Ni	0.90669300	2.29467600	0.66826800
H	-0.08334800	3.05274700	-0.36486400

[(PN)Ni]$_2$C$_6$H$_8$ (**1**)
(M06-L/6-31G**[LANL2DZ for Ni])
Electronic Energy = -3579.756404
Electronic and Zero-Point Energy = -3578.398591
Enthalpy = -3578.321971
Free Energy = -3578.506301
M06-L/def2-TZVP
Electronic Energy = -6258.505163

Ni	-1.12904900	5.59808000	4.62911200
P	-2.17973100	5.92592800	2.75779100
N	0.25600900	4.87828800	3.44151700
N	-1.12025200	5.33797700	1.59461900
C	-0.02413700	4.80218300	2.12073900
C	-1.79695300	5.17484000	6.48247600
H	-2.34896900	4.23462500	6.42955100
C	-2.37277900	6.38898400	5.95395400
H	-3.44396100	6.37048200	5.77095200
C	-1.82439800	7.72685900	6.40366400
H	-2.33622800	8.02006400	7.33419300
H	-2.08958300	8.50554600	5.67670700
C	-2.50802100	7.69096900	2.22308500
C	-1.23117200	8.43434700	2.63878300
H	-1.05879600	8.37040600	3.72041900

H	-0.35252100	8.01630600	2.13544200
H	-1.30877100	9.49331900	2.36401100
C	-3.71238300	8.27505300	2.95610800
H	-4.65333000	7.83430500	2.60977300
H	-3.64647800	8.12601400	4.04094700
H	-3.77342300	9.35472400	2.77320700
C	-2.67549100	7.82581500	0.70945400
H	-3.62687400	7.42134500	0.35632300
H	-2.65041500	8.88799200	0.43621600
H	-1.86866800	7.31318400	0.17944400
C	-3.68093800	4.79839200	2.59087300
C	-3.11803800	3.37665100	2.69565700
H	-2.46063200	3.13577900	1.85518100
H	-2.54484900	3.24679900	3.62282700
H	-3.94373300	2.65504600	2.70737900
C	-4.66938900	5.00053700	3.73947900
H	-5.03138100	6.03009500	3.82526400
H	-5.54521500	4.35826800	3.58338400
H	-4.22742000	4.71354400	4.69865200
C	-4.37542900	4.97546000	1.24307000
H	-4.91718100	5.92516100	1.18327000
H	-3.66049600	4.93060200	0.41517300
H	-5.11086500	4.17386100	1.10018600
C	0.84228900	4.06012200	1.15136500
C	0.19758400	3.42285500	0.07919900
H	-0.87893800	3.53564400	-0.00856900
C	0.91167800	2.67362200	-0.84684500
H	0.38651500	2.18122800	-1.66082300
C	2.29558000	2.55949300	-0.73565700
H	2.85843400	1.97734800	-1.46027700
C	2.95214600	3.20320500	0.30871800
H	4.03264600	3.13389300	0.39904100
C	2.23603200	3.93908000	1.24897500
H	2.77682300	4.42711600	2.05092600
C	1.39192500	4.30012400	4.05599500
C	2.38370100	5.16597500	4.57838000
C	3.44232000	4.61366100	5.29913200
H	4.20606400	5.26641300	5.71533000
C	3.53480400	3.23887800	5.50207700
H	4.36434300	2.82626500	6.07018500
C	2.56070300	2.39984100	4.97671400
H	2.63246200	1.32620200	5.13908800
C	1.48048200	2.90669900	4.24884900
C	2.28219200	6.65882400	4.33327900
H	1.22062300	6.91855700	4.46506900
C	2.63898800	7.03137600	2.89235200

H	2.56448000	8.11475700	2.74623400
H	3.66793500	6.73535100	2.65530500
H	1.97558800	6.55407100	2.16653300
C	3.11241500	7.50535100	5.29064800
H	2.87490800	8.56620800	5.16157800
H	2.94112700	7.24930500	6.34191100
H	4.18568400	7.39319700	5.09834600
C	0.39807500	1.97313500	3.74793100
H	-0.18425300	2.50159500	2.98654300
C	0.95400400	0.71528000	3.09015900
H	0.14364600	0.11783000	2.66023000
H	1.65182000	0.96648200	2.28490800
H	1.48214000	0.07414100	3.80487200
C	-0.56000800	1.63996800	4.88890600
H	-1.37915300	0.99359100	4.55264600
H	-0.03901200	1.12789200	5.70695900
H	-1.00355500	2.55485100	5.30339700
C	-0.33719900	5.17506800	6.57094400
H	0.21493300	4.23511800	6.62708100
C	0.23832200	6.39120500	7.09528600
H	1.30949200	6.37358100	7.27853000
C	-0.31015300	7.72733600	6.64051500
H	0.20160900	8.01700700	5.70885200
H	-0.04495600	8.50880000	7.36448400
Ni	-1.00528100	5.60483800	8.42286300
P	0.04471200	5.94050100	10.29303500
N	-2.39019200	4.88845800	9.61262900
N	-1.01480700	5.35647000	11.45812500
C	-2.11040800	4.81785600	10.93381100
C	0.37165900	7.70784400	10.82101200
C	-0.90593200	8.44856900	10.40285400
H	-1.07862500	8.38043500	9.32153000
H	-1.78405400	8.03162900	10.90802200
H	-0.82917400	9.50862900	10.67364200
C	1.57538400	8.29020500	10.08558100
H	2.51677200	7.85148900	10.43329900
H	1.50938200	8.13714000	9.00130300
H	1.63559600	9.37058800	10.26450900
C	0.53923700	7.84852300	12.33411200
H	1.49108700	7.44636100	12.68858700
H	0.51311200	8.91169200	12.60336800
H	-0.26698200	7.33704800	12.86615500
C	1.54664000	4.81469000	10.46473600
C	0.98471500	3.39214500	10.36579800
H	0.32737600	3.15436700	11.20721100
H	0.41169100	3.25802500	9.43913200

H	1.81088300	2.67103900	10.35717200
C	2.53487400	5.01291400	9.31525300
H	2.89629800	6.04233700	9.22547300
H	3.41106600	4.37172500	9.47370500
H	2.09287600	4.72208100	8.35723900
C	2.24098800	4.99779400	11.81179200
H	2.78210700	5.94808900	11.86767400
H	1.52609100	4.95588100	12.63987700
H	2.97696100	4.19728800	11.95799300
C	-2.97654000	4.07899900	11.90590600
C	-2.33161600	3.44649500	12.98075700
H	-1.25520700	3.56048500	13.06835300
C	-3.04535800	2.70038500	13.90959000
H	-2.52001000	2.21165300	14.72565400
C	-4.42914000	2.58471400	13.79850100
H	-4.99172100	2.00499600	14.52527200
C	-5.08593900	3.22375800	12.75141000
H	-6.16636000	3.15322800	12.66107500
C	-4.37016300	3.95647800	11.80843400
H	-4.91112400	4.44088200	11.00439700
C	-3.52579900	4.30745500	9.00025000
C	-4.51799300	5.17083900	8.47456600
C	-5.57635400	4.61525900	7.75593100
H	-6.34043500	5.26606200	7.33730500
C	-5.66811300	3.23967800	7.55813900
H	-6.49743300	2.82449500	6.99158200
C	-4.69356700	2.40312500	8.08663800
H	-4.76473800	1.32884600	7.92829200
C	-3.61363100	2.91327400	8.81261200
C	-4.41713100	6.66468900	8.71382700
H	-3.35574300	6.92443200	8.58050800
C	-4.77355100	7.04275500	10.15340700
H	-4.69943400	8.12673600	10.29522400
H	-5.80229700	6.74726400	10.39197600
H	-4.10972200	6.56859500	10.88088400
C	-5.24821600	7.50705300	7.75352200
H	-5.01100300	8.56850800	7.87814500
H	-5.07751800	7.24679300	6.70320000
H	-6.32132900	7.39530000	7.94693700
C	-2.53077300	1.98216800	9.31708500
H	-1.94908600	2.51363200	10.07687200
C	-3.08610000	0.72617500	9.97894700
H	-2.27551000	0.13082200	10.41133500
H	-3.78449500	0.97964700	10.78298000
H	-3.61340900	0.08217500	9.26620000
C	-1.57206500	1.64571900	8.17760600

H	-0.75257000	1.00112600	8.51641800
H	-2.09239100	1.13037500	7.36117600
H	-1.12906900	2.55945900	7.76001400

References

1. C. M. Kelly, J. T. Fuller, C. M. Macaulay, R. McDonald, M. J. Ferguson, S. M. Bischof, O. L. Sydora, D. H. Ess, M. Stradiotto and L. Turculet, *Angew. Chem. Int. Ed.*, 2017, **56**, 6312-6316.

2. C. M. Macaulay, S. J. Gustafson, J. T. Fuller, D. H. Kwon, T. Ogawa, M. J. Ferguson, R. McDonald, M. D. Lumsden, S. M. Bischof, O. L. Sydora, D. H. Ess, M. Stradiotto and L. Turculet, *ACS Catal.*, 2018, **8**, 9907-9925.

3. C. M. Macaulay, T. Ogawa, R. McDonald, O. L. Sydora, M. Stradiotto and L. Turculet, *Dalton Trans.*, 2019, **48**, 9581-9587.

4. M. Weber, C. Hellriegel, A. Rueck, J. Wuethrich, P. Jenks and M. Obkircher, *Anal. Bioanal. Chem.*, 2015, **407**, 3115-3123.

5. (a) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284−298. (b) Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* **2006**, *125*, 194101. (c) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215−241. (d) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157−167.