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Electronic Supplementary Information

For

Interrogating the steric outcome during H2 heterolysis: in-plane steric effects in the regioselective protonation of the PN3P-pincer ligand

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1. General Procedures

All experiments (if not mentioned otherwise) with metal complexes were carried out under an atmosphere of dry argon in a glovebox or using standard Schlenk techniques. All glassware was rigorously dried. All solvents were distilled from sodium benzophenone ketyl prior to use. All other chemicals were commercially available and used as received. Complexes **1** and **4** were prepared according to the literature procedure.[1] NMR spectra were recorded at 400 MHz (^{1}H), 101 MHz (^{13}C), and 162 MHz (^{31}P) using a Bruker Avance-400 NMR spectrometer, 500 MHz (^{1}H), 126 MHz (^{13}C) and 202 MHz (^{31}P) using a Bruker Avance-500 NMR spectrometer, and 600 MHz (^{1}H), 151 MHz (^{13}C) and 243 MHz (^{31}P) using a Bruker Avance-600 NMR spectrometer. All spectra were recorded at 25 °C. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents (7.16 ppm, C_6D_6), and the ^{13}C NMR chemical shifts were referenced to the ^{13}C signals of the deuterated solvents (128.06 ppm, C_6D_6). Elemental analyses were carried out on a Flash 2000 elemental analyzer. The X-ray diffraction data were collected using Bruker-AXS KAPPA-APEXII CCD diffractometer. CCDC 1891945 (**2**), 1891946 (**3**), 1891947 (**4**), 1891951 (**5**) and 1891954 (**7b**) contain supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of complex 2

A C_6D_6 solution (0.5 mL) of $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol) was added to the C_6D_6 solution (0.5 mL) of complex **1** (11.1 mg, 20.0 μmol), the color of the mixture immediately changed from red to brown. The resulting solution was directly used to NMR analysis. The crystals suitable for X-ray diffraction analysis were grown from a concentrated C_6D_6 solution at room temperature (16.4 mg, 76.8%). ^{1}H NMR (500 MHz, Benzene-d_6) δ = 5.14 (t, J = 3.5 Hz, 1H, –C(Et)=C*H*–), 2.27 (q, J = 7.4 Hz, 2H, –C*H*$_2$CH$_3$), 1.77 (dq, J = 14.6 Hz, 7.3 Hz, 2H, –C*H*$_2$CH$_3$), 1.14 (dt, J = 11.5 Hz, 4.4 Hz, 36H, –PC(C*H*$_3$)$_3$), 1.10-1.05 (m, 2H, –C*H*$_2$CH$_3$), 0.94 (t, J = 7.4 Hz, 3H, –CH$_2$C*H*$_3$), 0.54 (t, J = 7.4 Hz, 6H, –CH$_2$C*H*$_3$), -0.11 (s, 1H, –O*H*); ^{31}P{^{1}H} NMR (202 MHz, Benzene-d_6) δ = 103.51 (d, J = 237.8 Hz, 1P), 103.16 (d, J = 237.8 Hz, 1P); ^{13}C{^{1}H} NMR (126 MHz, Benzene-d_6) δ = 182.03 (d, J = 7.7 Hz, –N=*C*–), 169.92 (d, J = 8.2 Hz, –N=*C*–), 149.84 (s, Ar-*C*), 147.95 (s, Ar-*C*), 141.50 (tt, J = 12.4 Hz, 5.9 Hz, Ar-*C*), 139.53 (dt, J = 19.6 Hz, 6.5 Hz, Ar-*C*), 138.66 (s, –C(Et)=C*H*–), 136.96–136.50 (m, Ar-*C*), 135.22 (dd, J = 13.5 Hz, 2.8 Hz, –*C*(Et)=CH–), 122.37-121.08 (m, Ar-*C*), 50.99 (dd, J = 11.4 Hz, 2.2 Hz, -*C*(Et)$_2$), 38.32 (ddd, J = 19.8 Hz, 12.8 Hz, 6.4 Hz, –P*C*(CH$_3$)$_3$), 36.04 (s, –C(*C*H$_2$CH$_3$)$_2$), 27.74 (d, J = 3.7 Hz, –PC(*C*H$_3$)$_3$), 27.05 (s, –C(*C*H$_2$CH$_3$)=CH–), 13.96 (s, –C(CH$_2$*C*H$_3$)=CH–), 9.93 (s, –C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{45}H_{53}BF_{15}N_3NiOP_2$: Calc. C, 50.59; H, 5.00; N, 3.93. Found: C, 50.91; H, 5.17; N, 3.76.

Synthesis of complex 3

A C_6D_6 solution (1 mL) of complex **2** (21.4 mg, 20.0 μmol) was put in a *J*-Young NMR tube. The tube was connected to a Schlenk line and then degassed and saturated with H_2 three times. The color of the solution turned from brown to light yellow immediately. The samples suitable for X-ray diffraction analysis were crystallized from a concentrated pentane solution at room temperature (17.6 mg, 82.0%). ^{1}H NMR (500 MHz, Benzene-d_6) δ = 9.41 (s, 1H, –N*H*=C–), 5.10 (s, 1H, –C(Et)=C*H*–), 2.75 (s, 1H, –O*H*), 2.32 (q, J = 7.4 Hz, 2H, –C*H*$_2$CH$_3$), 2.08 (dq, J = 14.5

Hz, 7.3 Hz, 2H, –CH_2CH$_3$), 1.16–1.08 (m, 20H, –CH$_2$CH_3, –PC(CH_3)$_3$), 1.06–0.94 (m, 21H, –PC(CH_3)$_3$, –CH$_2$CH_3), 0.40 (t, *J* = 7.4 Hz, 6H, –CH$_2$CH_3), -16.20 (dd, *J* = 60.6 Hz, 54.6 Hz, 1H, Ni–*H*); ^{31}P{^{1}H} NMR (202 MHz, Benzene-d_6) δ = 147.46 (d, *J* = 223.8 Hz, 1P), 144.89 (d, *J* = 223.8 Hz, 1P); ^{13}C{^{1}H} NMR (151 MHz, Benzene-d_6) δ = 182.31 (t, *J* = 7.5 Hz, –NH=*C*–), 165.22 (d, *J* = 8.0 Hz, –N=*C*–), 149.85–149.39 (m, Ar-*C*), 148.25–147.88 (m, Ar-*C*), 141.34 (s, –C(Et)=C*H*–), 140.47–140.02 (m, Ar-*C*), 138.84–138.10 (m, Ar-*C*), 136.96–136.46 (m, Ar-*C*), 134.75 (d, *J* = 14.9 Hz, –*C*(Et)=CH–), 50.08 (d, *J* = 3.5 Hz, –*C*(Et)$_2$), 37.24 (d, *J* = 13.2 Hz, –P*C*(CH$_3$)$_3$), 36.08 (dd, *J* = 21.7 Hz, 3.3 Hz, –P*C*(CH$_3$)$_3$), 32.74 (s, –C(*C*H$_2$CH$_3$)$_2$), 28.28 (d, *J* = 6.3 Hz, –PC(*C*H$_3$)$_3$), 27.94 (d, *J* = 4.8 Hz, –PC(*C*H$_3$)$_3$), 26.17 (s, –C(*C*H$_2$CH$_3$)=CH–), 13.90 (s, –C(CH$_2$*C*H$_3$)=CH–), 9.20 (s, –C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{45}H_{55}BF_{15}N_3NiOP_2$: Calc. C, 50.50; H, 5.18; N, 3.93. Found: C, 50.72; H, 5.30; N, 3.81.

Synthesis of complex 5

A C_6D_6 solution (1 mL) of complex **4** (13.8 mg, 20.0 μmol) was put in a *J*-Young NMR tube. The tube was connected to a Schlenk line and degassed and saturated with H_2 three times, and then was heated to 50 °C for 12 h. The color of the solution turned from red to light yellow. The samples suitable for X-ray diffraction analysis were crystallized from a concentrated pentane solution at room temperature. ^{1}H NMR (400 MHz, Benzene-d_6) δ = 10.08 (s, 1H, N*H*), 5.60 (t, *J* = 2.6 Hz, 1H, –C(Et)=C*H*–), 2.90 (dq, *J* = 14.6 Hz, 7.3 Hz, 2H, –CH_2CH$_3$), 2.39 (qd, *J* = 7.4 Hz, 1.0 Hz, 2H, –CH_2CH$_3$), 1.74 (dq, *J* = 15.0 Hz, 7.6 Hz, 2H, –CH_2CH$_3$), 1.32 (dd, *J* = 13.7 Hz, 1.9 Hz, 18H, –PC(CH_3)$_3$), 1.17–0.91 (m, 21H, –PC(CH_3)$_3$, –CH_2CH$_3$), 0.60 (t, *J* = 7.4 Hz, 6H, –CH$_2$CH_3), -16.19 (dd, *J* = 59.9 Hz, 55.5 Hz, 1H, –Ni*H*). ^{31}P{^{1}H} NMR (162 MHz, Benzene-d_6) δ = 146.09 (d, *J* = 223.7 Hz, 1P), 143.87 (d, *J* = 223.7 Hz, 1P). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ = 182.99 (t, *J* = 7.6 Hz, –NH=*C*–), 165.78 (dd, *J* = 7.4 Hz, 1.4 Hz, –N=*C*–), 142.53 (s, –C(Et)=*C*H–), 134.29 (d, *J* = 13.9 Hz, –*C*(Et)=CH–), 50.72 (d, *J* = 3.6 Hz, –*C*(Et)$_2$), 37.46 (dd, *J* = 12.9 Hz, 3.5 Hz, –P*C*(CH$_3$)$_3$), 36.04 (dd, *J* = 20.1 Hz, 5.4 Hz, –P*C*(CH$_3$)$_3$), 33.00 (s, –C(*C*H$_2$CH$_3$)$_2$), 28.84 (d, *J* = 6.2 Hz, –PC(*C*H$_3$)$_3$), 28.00 (d, *J* = 4.6 Hz, –PC(*C*H$_3$)$_3$), 26.29 (s, –C(*C*H$_2$CH$_3$)=CH–), 14.00(s, –C(CH$_2$*C*H$_3$)=CH–) , 9.47 (s, –C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{28}H_{54}F_3N_3NiO_3P_2S$: Calc. C, 48.71; H, 7.88; N, 6.09. Found: C, 48.93; H, 8.05; N, 5.91.

Synthesis of complex 6

AgOTf (308 mg, 1.2 mmol) was added to the toluene solution of (PN^{3}P)^{2Et}NiCl (10 mL, 547 mg, 1.0 mmol), which is a byproduct of the synthesis of (PN^{3}P)^{3Et}NiCl and separated by column chromatography.[2] The resulting suspension was stirred for 24 h at 50 °C, filtered and all the volatiles were removed in *vacuo* to yield a red solid (621 mg, 94.0%). The samples suitable for X-ray diffraction analysis were crystallized from a concentrated pentane solution at room temperature. ^{1}H NMR (500 MHz, Benzene-d_6) δ = 6.25 (d, *J* = 9.7 Hz, 1H, C(Et)$_2$–CH=C*H*–), 5.26 (dt, *J* = 9.7 Hz, 3.1 Hz, 1H, –C(Et)$_2$-C*H*–), 1.85 (dq, *J* = 14.6 Hz, 7.4 Hz, 2H, –CH_2CH$_3$), 1.52 (dd, *J* = 13.6 Hz, 2.6 Hz, 36H, –PC(CH_3)$_3$), 1.11 (dq, *J* = 14.8 Hz, 7.5 Hz, 2H, –CH_2CH$_3$), 0.57 (t, *J* = 7.4 Hz, 6H, –CH$_2$CH_3). ^{31}P{^{1}H} NMR (202 MHz, Benzene-d_6) δ = 112.16 (d, *J* = 250.3 Hz, 1P), 109.08 (d, *J*=250.3 Hz, 1P). ^{13}C{^{1}H} NMR (126 MHz, Benzene-d_6) δ = 181.98 (d, *J* = 9.5 Hz, –N=*C*–), 170.01 (d, *J* = 9.8 Hz, –N=*C*–), 144.58 (s, –C(Et)$_2$–*C*H–), 122.40 (d, *J* = 18.9 Hz, –C(Et)$_2$–CH=*C*H–), 118.85 (q, *J* = 319.0 Hz, –*C*F$_3$), 49.95 (d, *J* = 14.2 Hz, –*C*(Et)$_2$),

38.49 (dt, J = 14.9 Hz,, 4.5 Hz, –P*C*$(CH_3)_3$), 35.92 (s, –C(*C*$H_2CH_3)_2$), 28.28 (dd, J = 31.8 Hz, 4.3 Hz, –P*C*$(CH_3)_3$), 9.68 (s, –C(CH_2*C*$H_3)_2$). Elemental analysis (%) for $C_{26}H_{48}F_3N_3NiO_3P_2S$: Calc. C, 47.29; H, 7.33; N, 6.36. Found: C, 47.46; H, 7.45; N, 6.28.

Synthesis of complex 7

The procedure is similar to that of complex **5** with a yield of 97.7% (**7a** and **7b**). **7b** suitable for X-ray diffraction analysis were crystallized from a concentrated pentane solution at room temperature. ^{1}H NMR (500 MHz, Benzene-d_6) For **7b** (main product): δ = 11.10 (s, 1H, N*H*), 7.69 (d, J = 9.8 Hz, 1H, –C(Et)$_2$CH=C*H*–),5.70 (d, J = 9.7 Hz, 1H, –C(Et)$_2$C*H*=CH–),1.76 (dq, J = 14.6 Hz, 7.4 Hz, 2H, –CH_2CH$_3$), 1.63–1.52 (m, 2H, –CH_2CH$_3$), 1.18 (d, J = 15.0 Hz, 18H, –PC(C$H_3)_3$), 1.06 (d, J = 14.0 Hz, 18H, –PC(C$H_3)_3$), 0.44 (t, J = 7.4 Hz, 6H, –CH$_2$CH_3), -16.28 (dd, J = 59.9 Hz, 55.9 Hz, 1H, –Ni*H*); For **7a** (by product): δ = 10.23 (s, 0.16H, N*H*), 6.40 (d, J = 9.9 Hz, 0.16H, –C(Et)$_2$CH=C*H*–), 5.37 (d, J = 9.9 Hz, 0.17H, –C(Et)$_2$C*H*=CH–), 2.85 (dq, J = 14.7 Hz, 7.3 Hz, 0.33H, –CH_2CH$_3$), 1.32–1.24 (m, 6.15H, –PC(C$H_3)_3$), 0.96–0.90 (m, 0.33H, –CH_2CH$_3$) 0.55 (t, J = 7.5 Hz, 1.08H, –CH$_2$CH_3), -16.20 (t, J = 57.6 Hz, 0.16H, –Ni*H*). ^{31}P{^{1}H} NMR (243 MHz, Benzene-d_6) For **7b** (main product): δ = 146.94 (d, J = 222.5 Hz), 143.46 (d, J = 222.4 Hz); For **7a** (by product): δ = 146.02 (m). ^{13}C{^{1}H} NMR (126 MHz, Benzene-d_6) For **7b** (main product): δ = 179.08 (d, J = 8.0 Hz, –N=C–), 169.91 (t, J = 8.7 Hz, –N=C–),154.75 (s, –C(Et)$_2$–*C*H=CH–), 116.89 (d, J = 6.2 Hz, –C(Et)$_2$–CH=*C*H–), 50.33 (d, J = 13.1 Hz, –*C*(Et)$_2$), 37.41–37.13 (m, –PC(*C*$H_3)_3$), 36.01 (s, –C(*C*$H_2CH_3)_2$), 35.98-35.78 (m, –PC(*C*$H_3)_3$), 28.22 (dd, J = 8.1 Hz, 5.8 Hz, –PC(*C*$H_3)_3$), 9.51(s, –C(CH_2*C*$H_3)_2$); For **7a** (by product): δ = 183.07-182.85 (m, –N=C–), 165.15–164.84 (m, –N=C–),147.94 (s, -C(Et)$_2$-*C*H=CH-), 120.99 (dd, J = 11.2 Hz, 5.9 Hz, -C(Et)$_2$-CH=*C*H-), 50.20-50.11 (m, –*C*(Et)$_2$), 37.48 (dd, J = 10.0 Hz, 6.3 Hz, –PC(*C*$H_3)_3$), 32.62 (s, –C(*C*$H_2CH_3)_2$), 28.82 (t, J = 3.7 Hz, –PC(*C*$H_3)_3$), 28.02 (t, J = 2.9 Hz, –PC(*C*$H_3)_3$), 9.36 (s, –C(CH_2*C*$H_3)_2$). Elemental analysis (%) for $C_{26}H_{50}F_3N_3NiO_3P_2S$: Calc. C, 47.14; H, 7.61; N, 6.34. Found: C, 47.37; H, 7.75; N, 6.16.

2. NMR Spectra

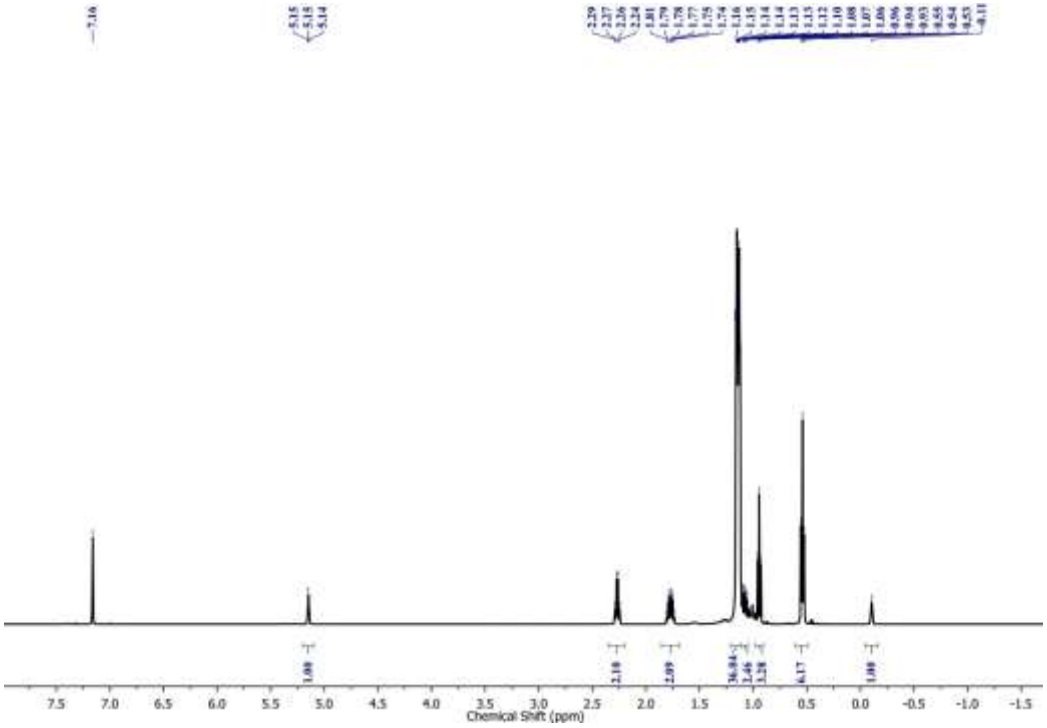

Fig. S1 ^{1}H NMR spectrum of complex **2** (500 MHz, Benzene-d_6).

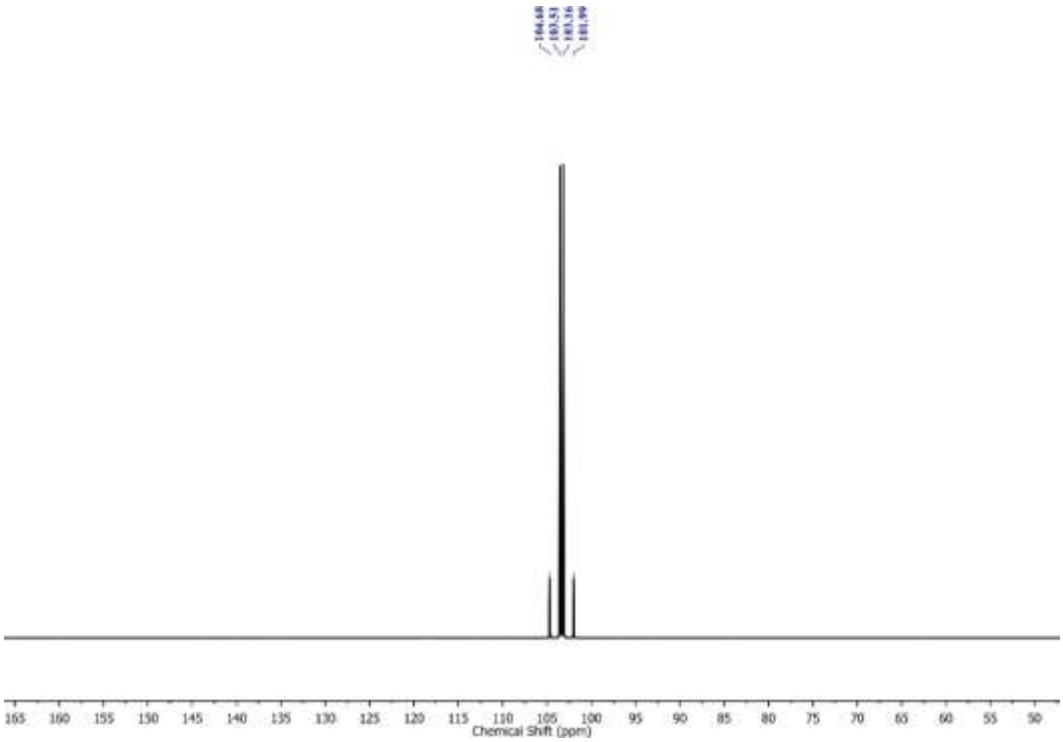

Fig. S2 ^{31}P{^{1}H} NMR spectrum of complex **2** (202 MHz, Benzene-d_6).

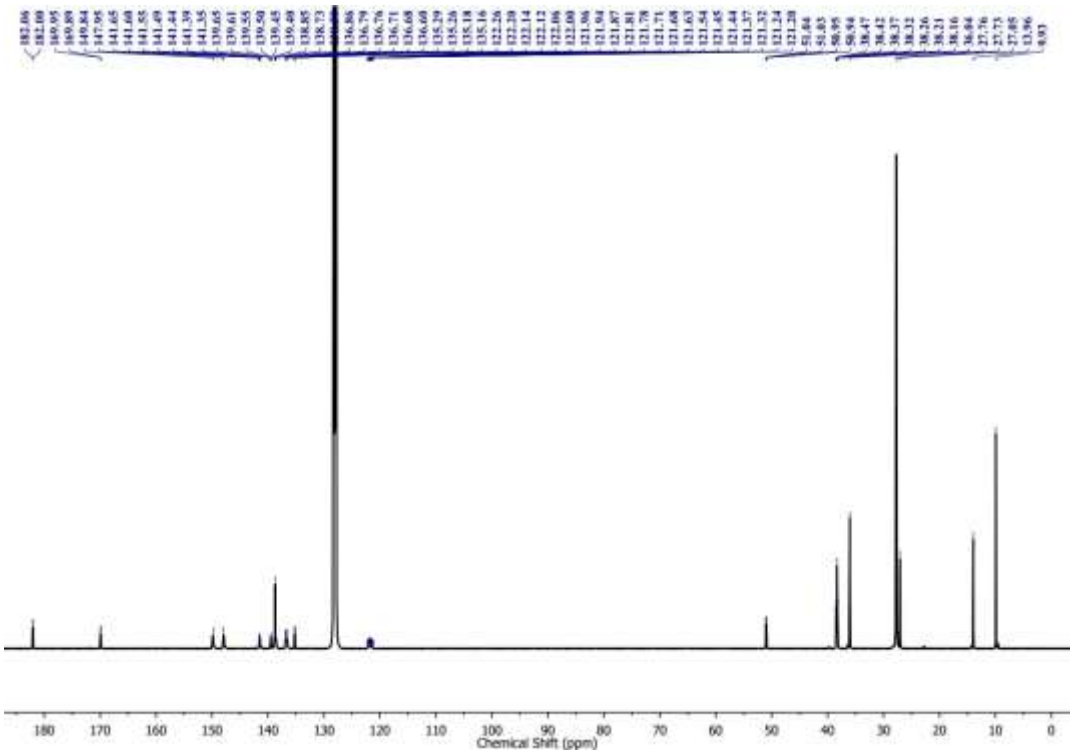

Fig. S3 $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** (126 MHz, Benzene-d_6).

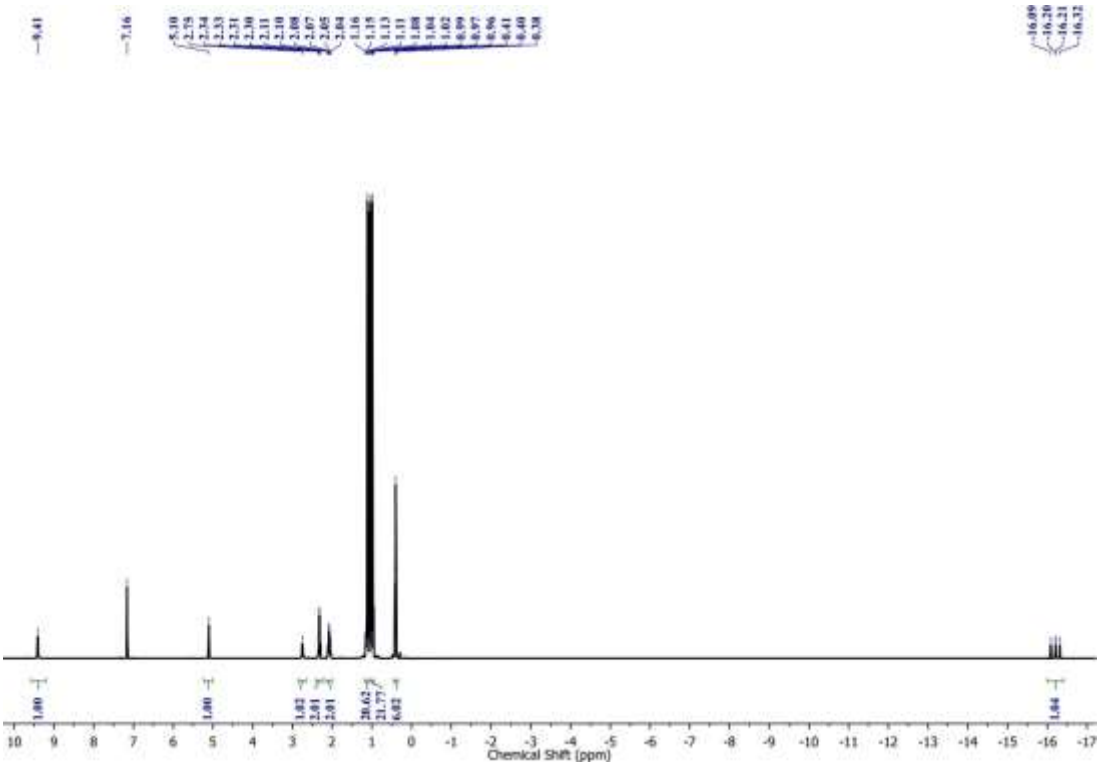

Fig. S4 ^{1}H NMR spectrum of complex **3** (500 MHz, Benzene-d_6).

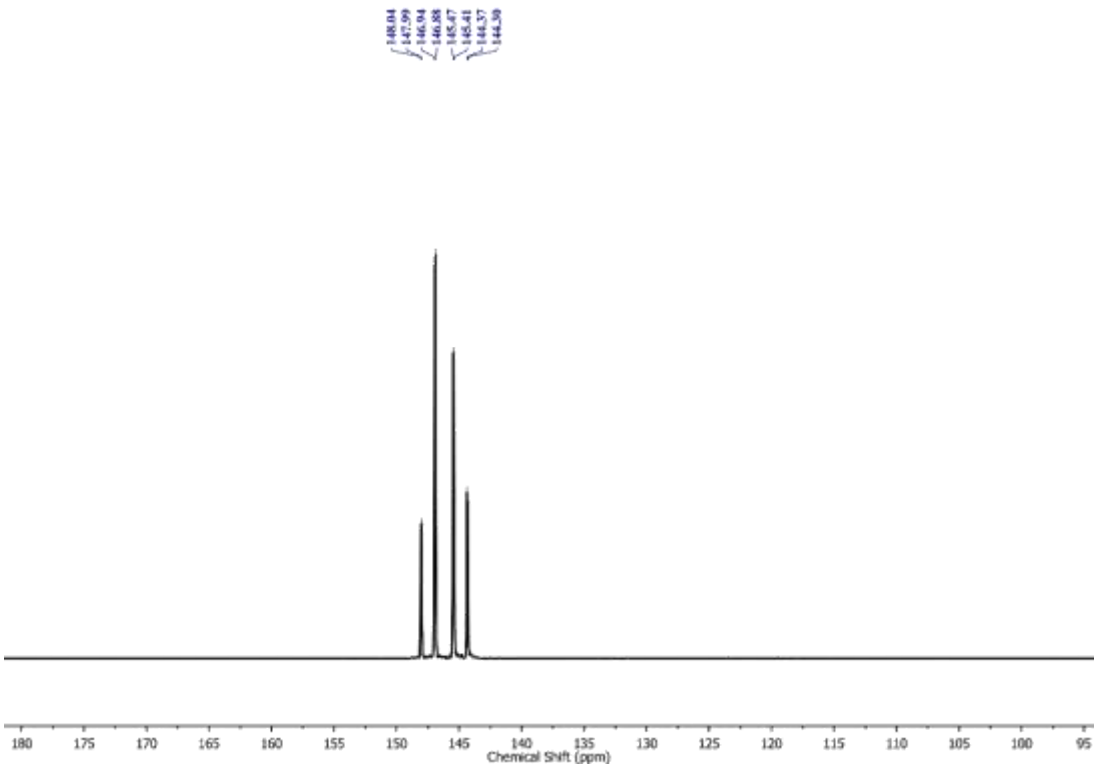

Fig. S5 $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** (202 MHz, Benzene-d_6).

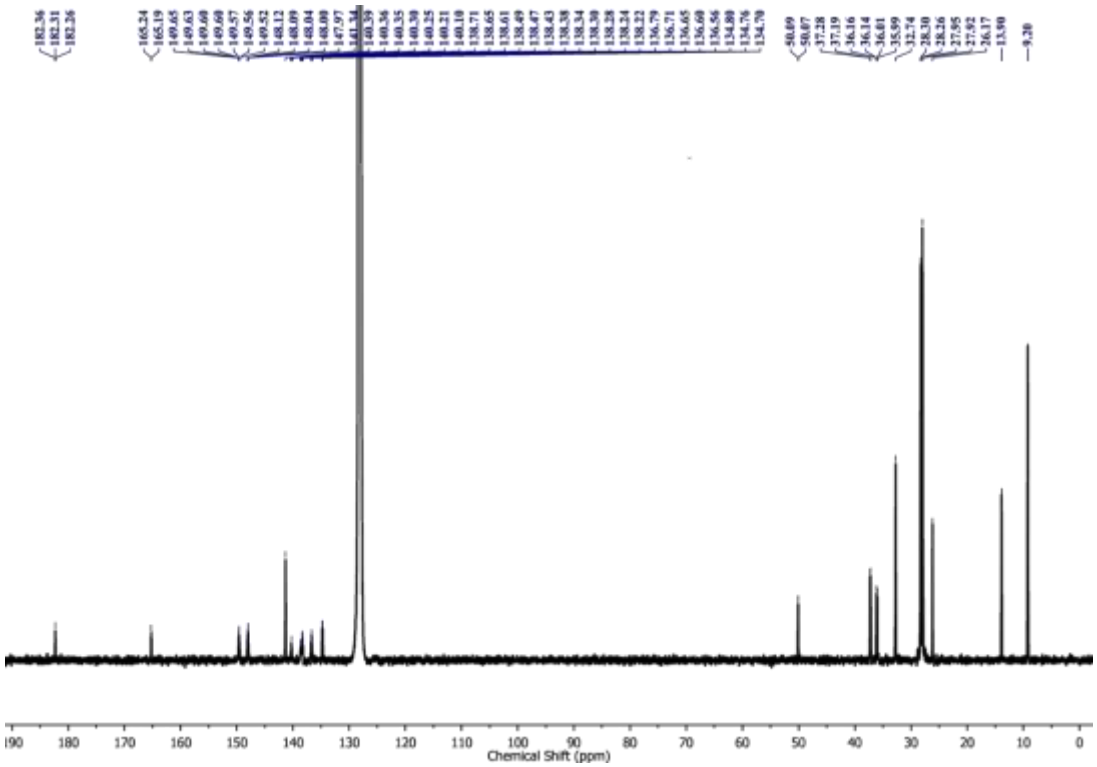

Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of complex **3** (151 MHz, Benzene-d_6).

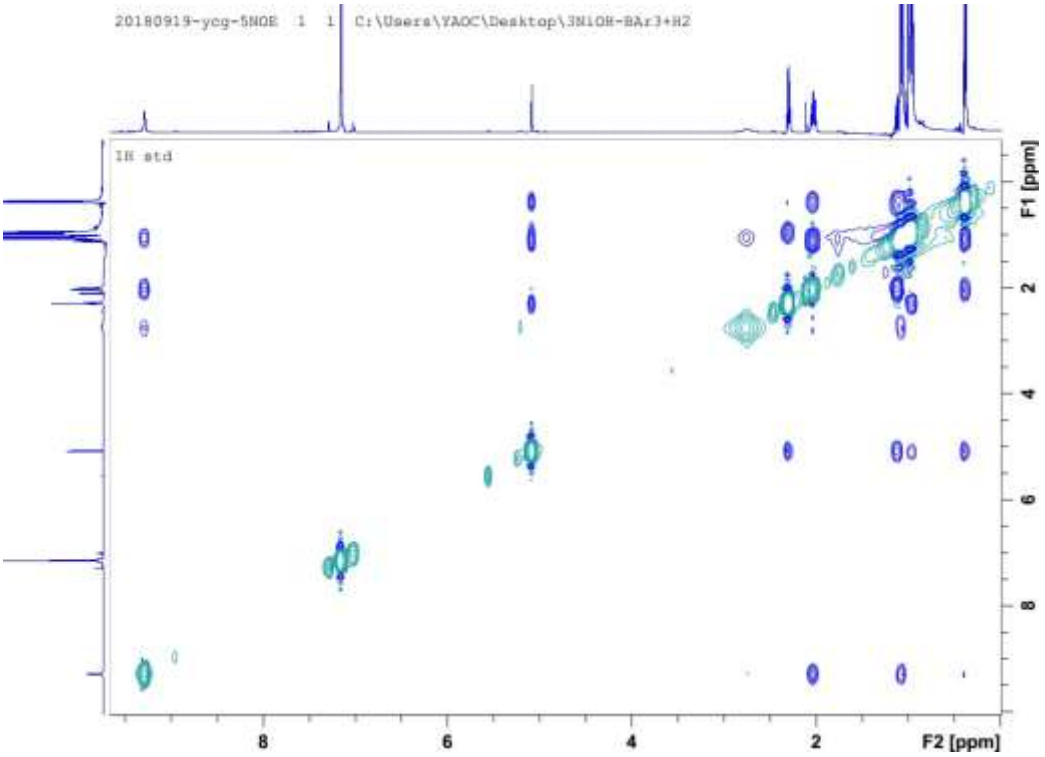

Fig. S7 2D-NOESY spectrum of complex **3** (600 MHz, 600 MHz, Benzene-d_6).

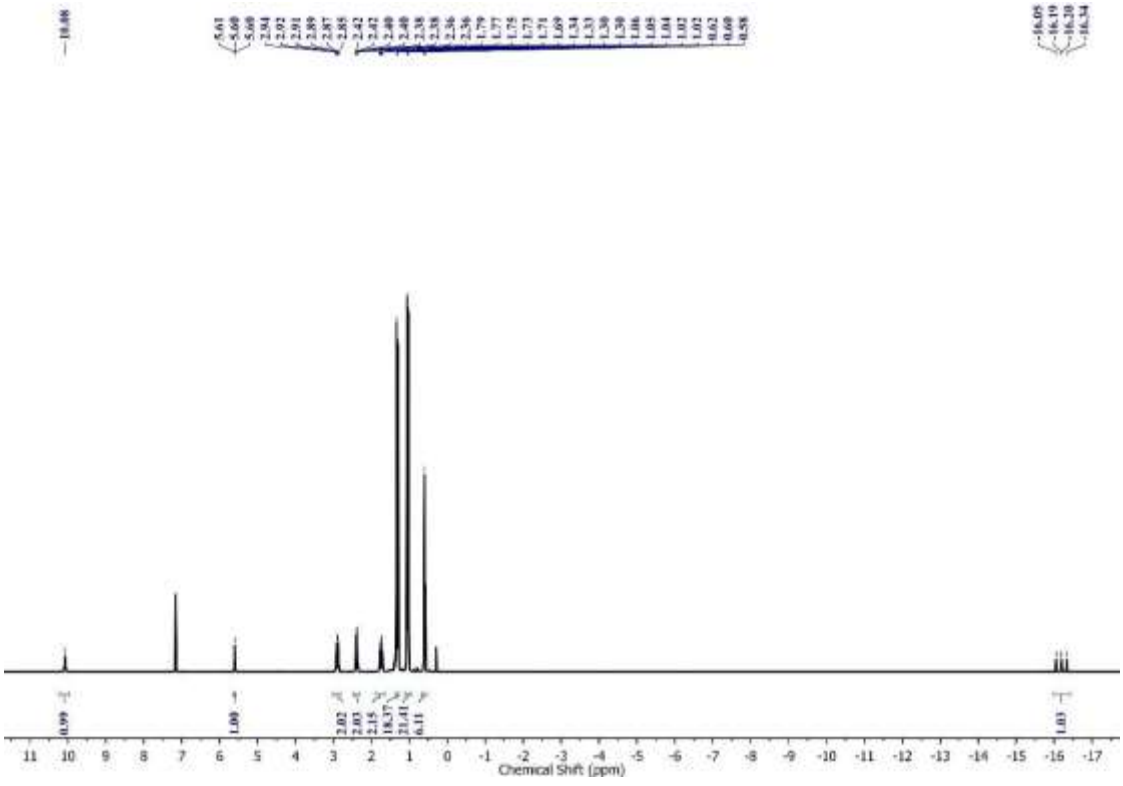

Fig. S8 ^{1}H NMR spectrum of complex **5** (400 MHz, Benzene-d_6).

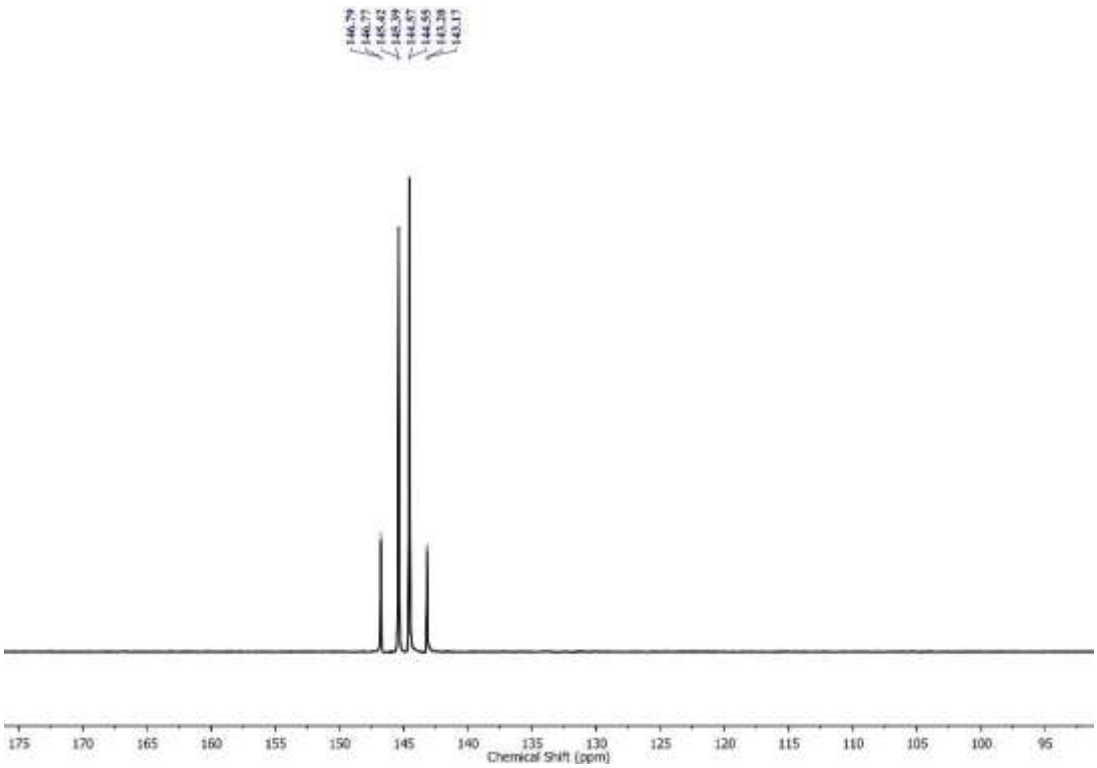

Fig. S9 $^{31}P\{^{1}H\}$ NMR spectrum of complex **5** (162 MHz, Benzene-d_6).

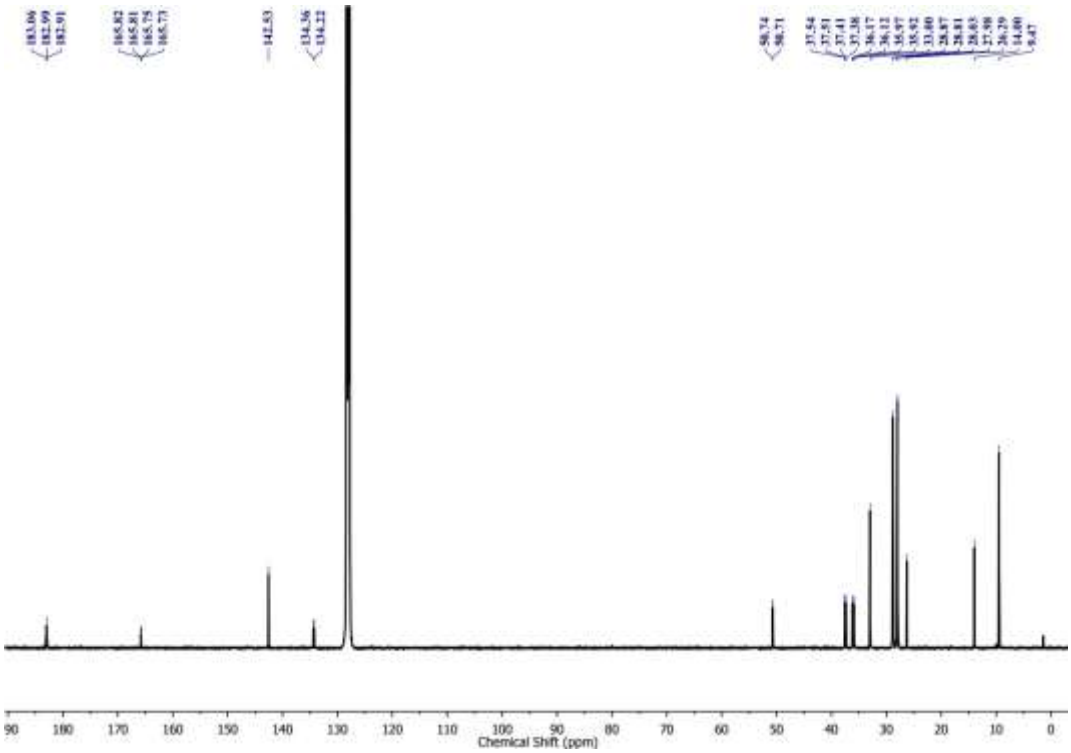

Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of complex **5** (101 MHz, Benzene-d_6).

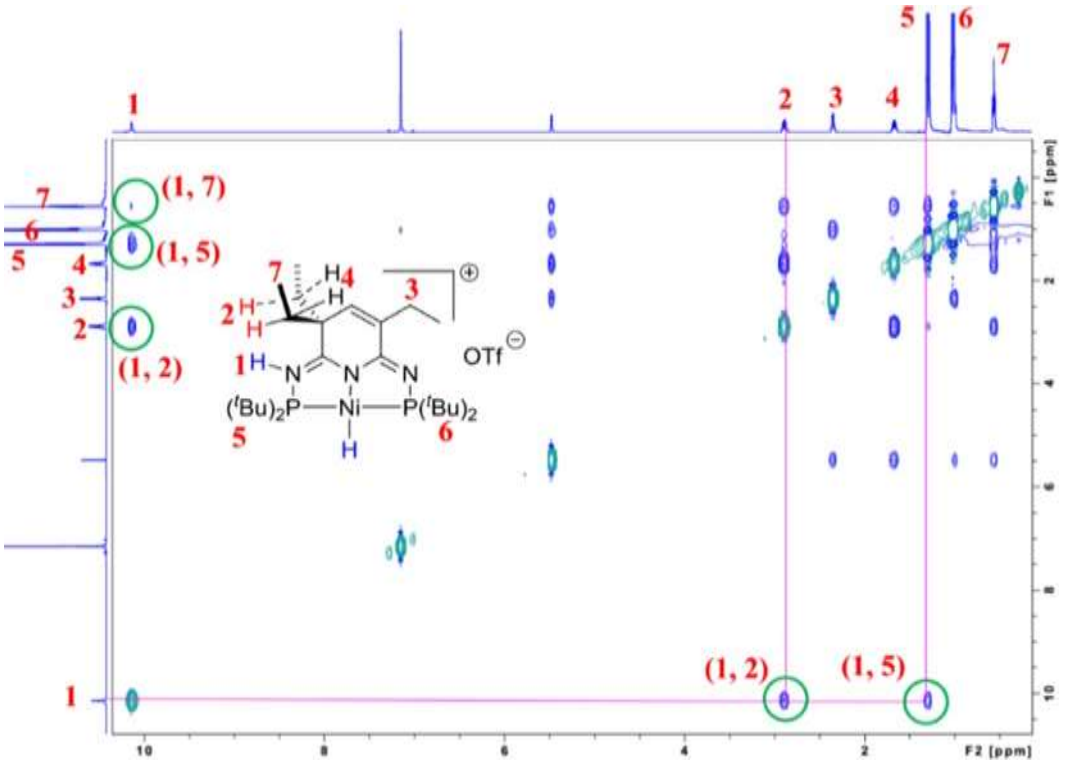

Fig. S11 2D-NOESY spectrum of complex **5** (600 MHz, 600 MHz, Benzene-d_6).

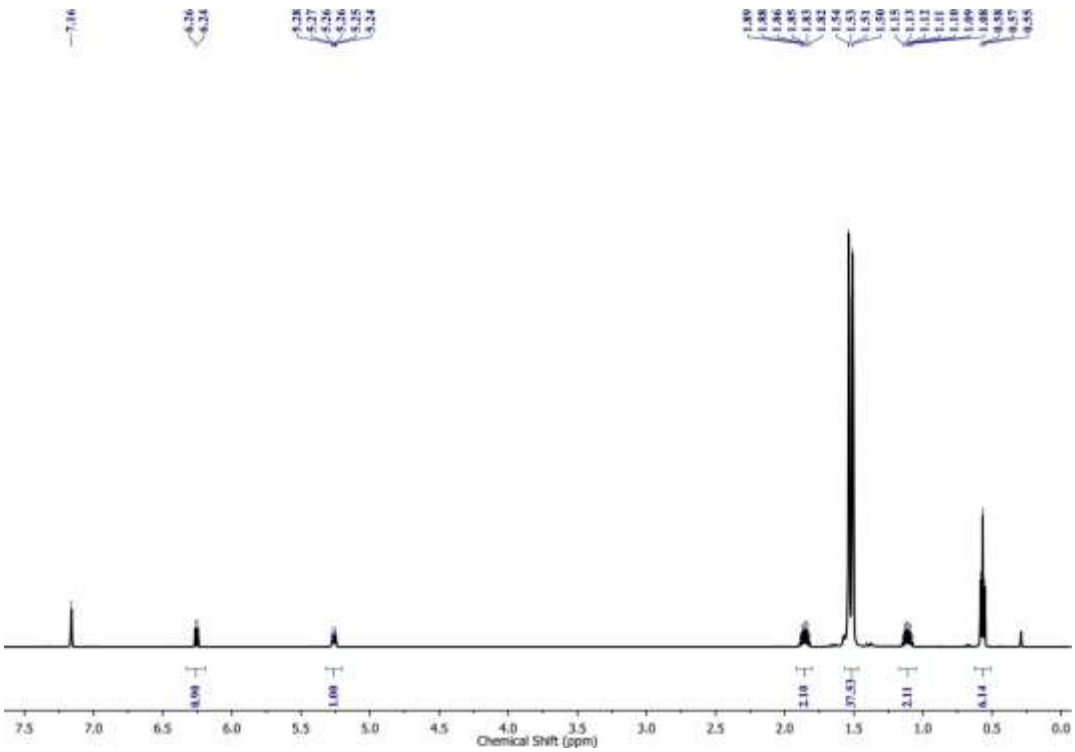

Fig. S12 ^{1}H NMR spectrum of complex **6** (500 MHz, Benzene-d_6).

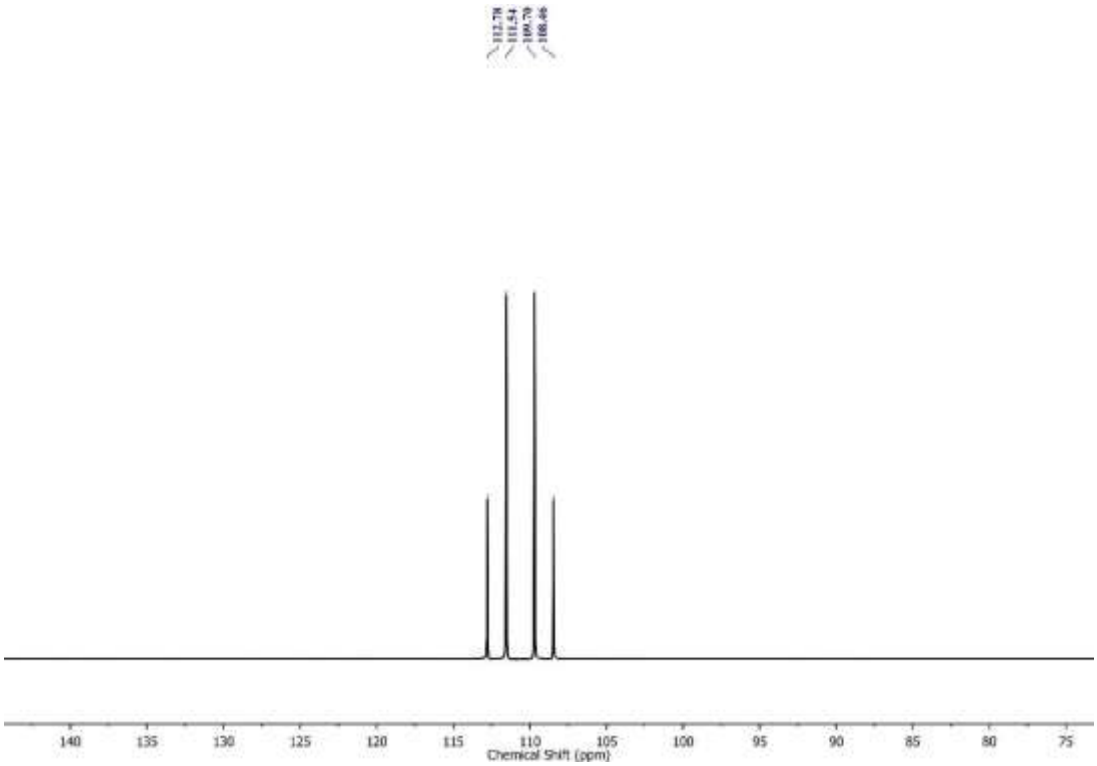

Fig. S13 $^{31}P\{^{1}H\}$ NMR spectrum of complex **6** (202 MHz, Benzene-d_6).

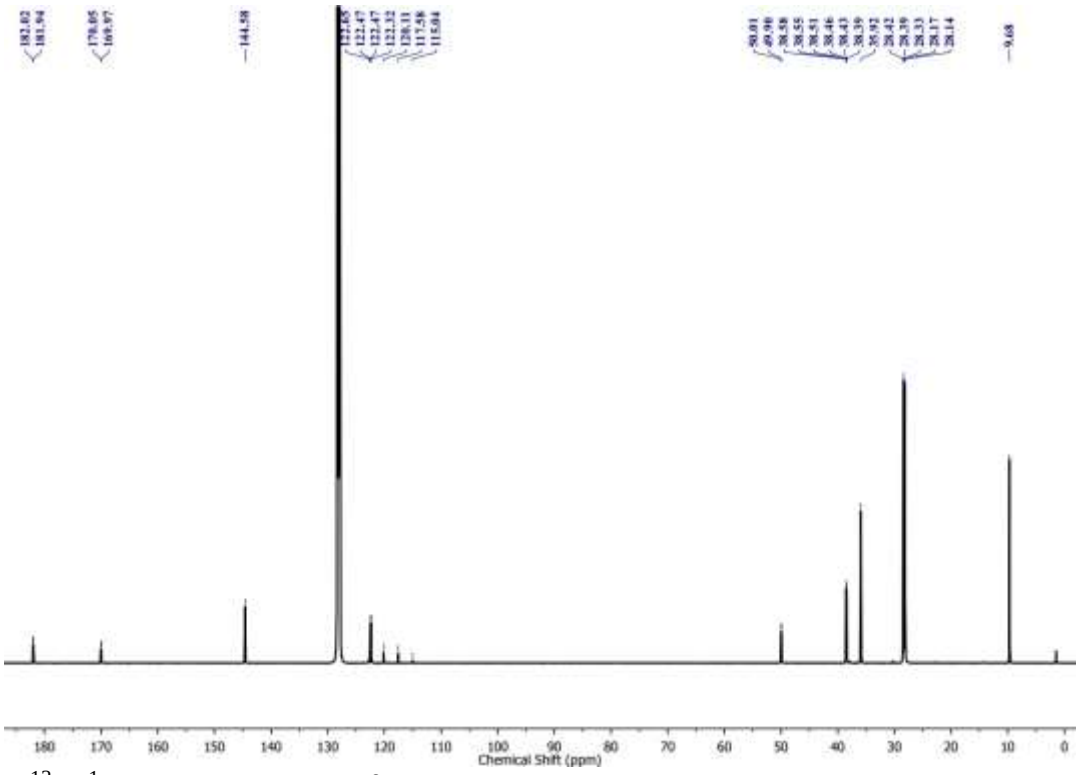

Fig. S14 $^{13}C\{^{1}H\}$ NMR spectrum of complex **6** (126 MHz, Benzene-d_6).

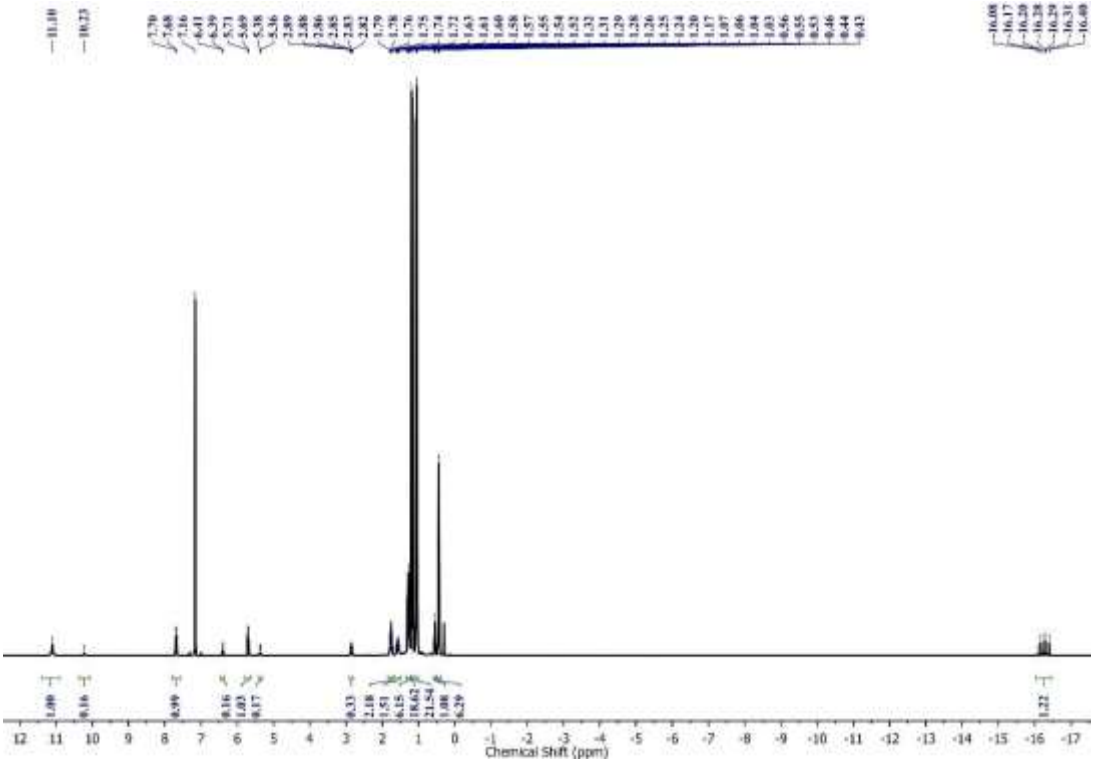

Fig. S15 ^{1}H NMR spectrum of complex **7** (500 MHz, Benzene-d_6).

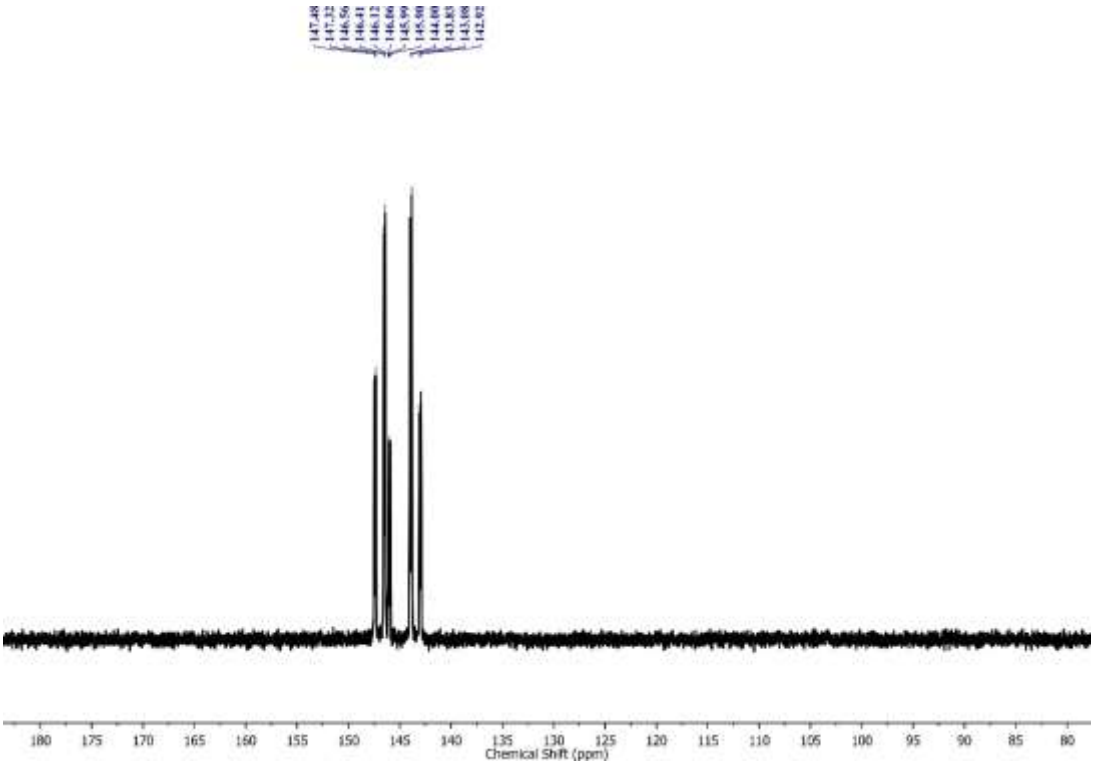

Fig. S16 ^{31}P{^{1}H} NMR spectrum of complex **7** (243 MHz, Benzene-d_6).

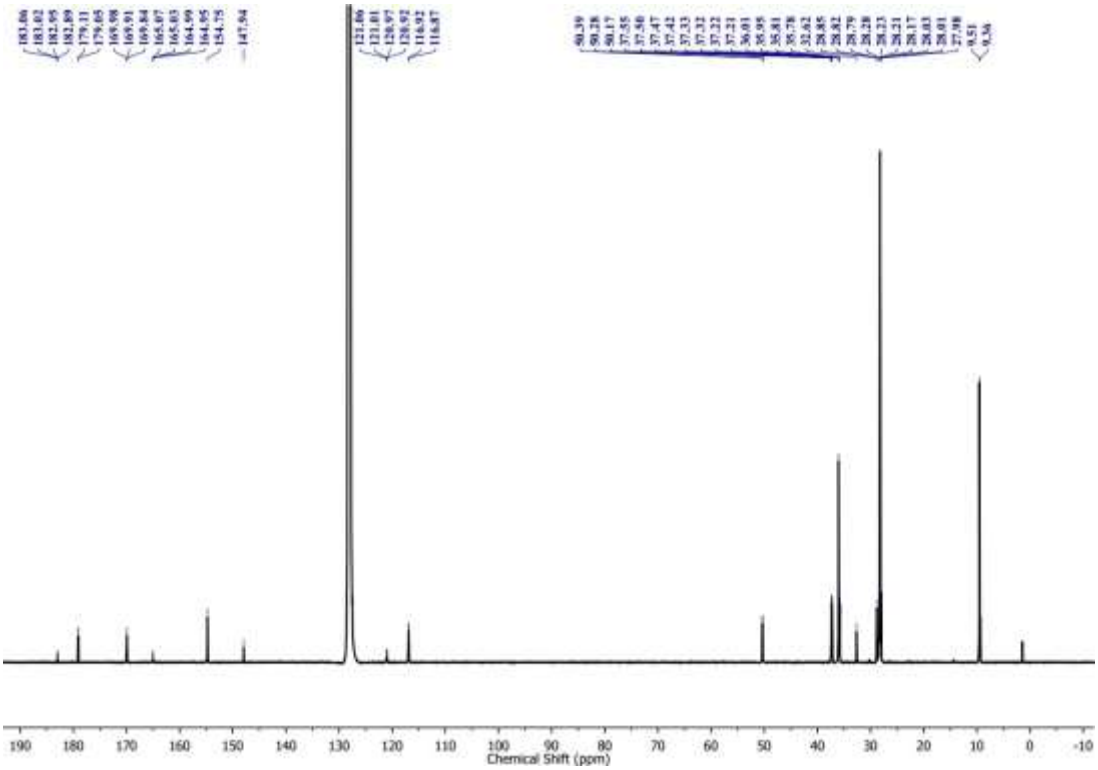

Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of complex **7** (126 MHz, Benzene-d_6).

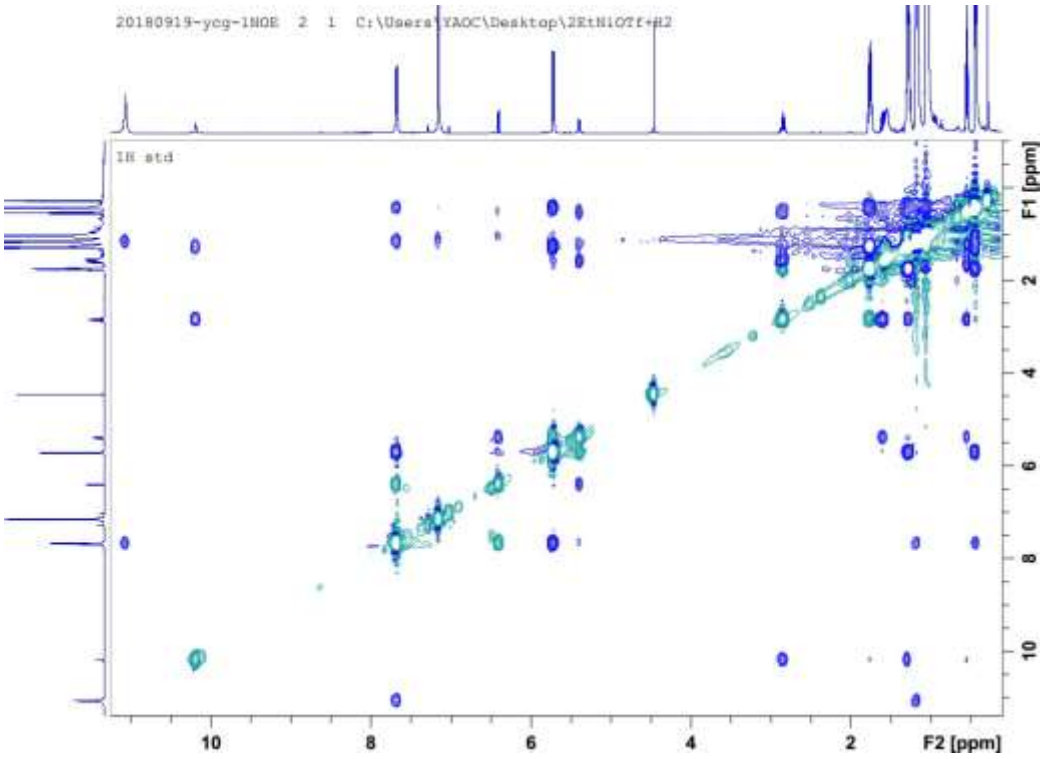

Fig. S18 2D-NOESY spectrum of complex **7** (600 MHz, 600 MHz, Benzene-d_6).

3. Summary of Crystallographic Data

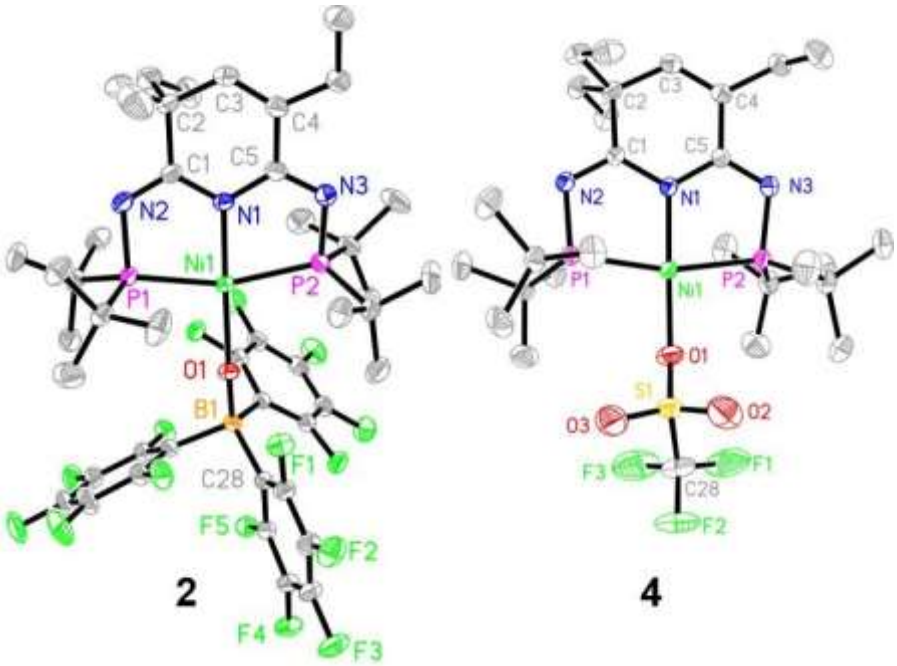

Fig. S19 Molecular structures of complexes **2** and **4**. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: For **2**): Ni(1)-N(1) 1.9373(19), Ni(1)-P(1) 2.2272(7), Ni(1)-P(2) 2.2156(7), Ni(1)-O(1) 2.0258(15), O(1)-H(1) 0.9300; N(1)-Ni(1)-O(1) 170.69(7), O(1)-Ni(1)-P(1) 98.70(5), O(1)-Ni(1)-P(2) 99.43(5), P(1)-Ni(1)-P(2) 160.70(3). For **4**): Ni(1)-N(1) 1.8878(11), Ni(1)-P(1) 2.2413(7), Ni(1)-P(2) 2.2239(7), Ni(1)-O(1) 1.9169(11); N(1)-Ni(1)-O(1) 175.30(4), O(1)-Ni(1)-P(1) 98.73(4), O(1)-Ni(1)-P(2) 95.77(4), P(1)-Ni(1)-P(2) 164.547(15).

Table S1 Summary of Crystallographic Data for complexes 2-5, 7b.

Entry	**2**	**3**	**4**	**5**	**7b**
Formula	$C_{45}H_{53}BF_{15}N_3NiOP_2$	$C_{45}H_{55}BF_{15}N_3NiOP_2$	$C_{28}H_{52}F_3N_3NiO_3P_2S$	$C_{31}H_{57}F_3N_3NiO_3P_2S$	$C_{26}H_{50}F_3N_3NiO_3P_2S$
F. W.	1068.36	1070.38	688.44	729.51	662.40
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P-1	P-1	P2(1)/n	P2(1)/c
a (Å)	19.7743(19)	9.3830(12)	8.583(3)	15.1132(18)	16.2124(13)
b (Å)	13.4867(13)	15.396(2)	17.582(6)	12.9640(17)	15.9077(14)
c (Å)	20.419(2)	18.138(2)	23.182(8)	19.891(3)	26.360(2)
α (deg)	90	83.562(4)	97.043(11)	90	90
β (deg)	118.011(5)	87.383(4)	90.899(11)	110.086(3)	95.740(3)
γ (deg)	90	86.027(4)	91.220(11)	90	90
V (Å ^{3})	4807.7(8)	2595.5(6)	3471(2)	3660.1(8)	6764.1(10)
Z	4	2	4	4	8
D_{calcd} (g/cm^3)	1.476	1.370	1.318	1.324	1.301
radiation (λ), Å	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)
θ range (°)	1.89 to 25.00	2.42 to 31.11	2.37 to 36.41	1.91 to 36.44	1.91 to 30.96
μ (mm^{-1})	0.567	0.525	0.759	0.724	0.776
F(000)	2200	1104	1464	1556	2816
no. of reflns collcd	57032	91445	195952	108987	121687
no. of reflns uniq	8462	16508	33672	17804	21410
R(int)	0.0448	0.0540	0.0776	0.0434	0.0396
GOF	1.079	1.071	1.033	1.046	1.035
R_1 [I> 2σ(I)]	0.0356	0.0392	0.0419	0.0279	0.0413
wR_2 [I> 2σ(I)]	0.0898	0.1008	0.1102	0.0697	0.1067
R_1 [all data]	0.0452	0.0455	0.0566	0.0352	0.0529
wR_2 [all data]	0.0960	0.1051	0.1198	0.0736	0.1141
Δ max, min/e Å $^{-3}$	0.545, -0.341	0.49, -0.69	1.080, -0.672	0.822, -0.476	2.121, -0.743

4. Computational Details

All calculations were performed with the Gaussian 09 suite of programs.[3] All the geometry optimizations were performed at B3LYP-D3[4] level of theory (with a mixed basis set BSI: 6-31G(d)[5] for C, H, N, P and LANL2DZ[6] for Ni which includes the relativistic effective core potential (ECP) of Hay and Wadt for Ni) together with UltraFine integration grid. Frequency calculations at the same level of theory on the above-mentioned optimized geometries were performed. The energies were then reevaluated by single point calculations on abovementioned optimized geometries using the same B3LYP-D3 functional with BSII: a larger basis set 6-311+G(2d,p) for C, H, N, P and also LANL2DZ for Ni. Solvation energies in benzene were also obtained by single point calculations at the B3LYP-D3/BSII level with a self-consistent reaction field (SCRF) [7] approach by using the intrinsic SMD[8] model. All images of the key optimized structures in this study were prepared by CYLview[9].

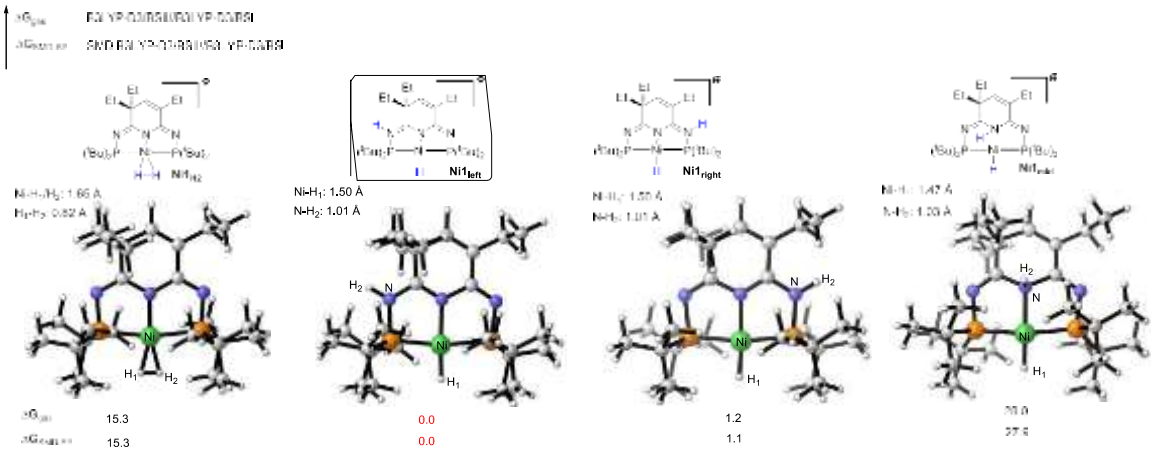

Fig. S20 The structures with relative Gibbs free energy data of the intermediates before and after H_2 splitting on the PN^3P-Ni species with three ethyl groups. (The energetics in the first and second line represent the energies in gas phase and in the experimental solvent (benzene) phase respectively.)

The Gibbs free energy for **Ni1$_{left}$** in which the proton binds to the N atom on the left arm side is the lowest and **Ni1$_{left}$** is set as the energy zero point. The counterpart **Ni1$_{right}$** with the proton connecting to the N atom on the right side is about 1.1-1.2 kcal/mol higher. This is consistent with the selectivity found in experiment that only **Ni1$_{left}$** was found and crystalized. While the relative Gibbs free energy for another intermediate **Ni1$_{mid}$** with the heterolysis assisted by the N atom connecting to the nickel center is extremely too high (27.9-28.0 kcal/mol). The initial **Ni1$_{H2}$** before H_2 splitting in which H_2 binds to the Ni center is 15.3 kcal/mol higher than **Ni1$_{left}$,** indicating the thermodynamic favorable property of the hydrogen cleavage in this Ni-Pincer complex.

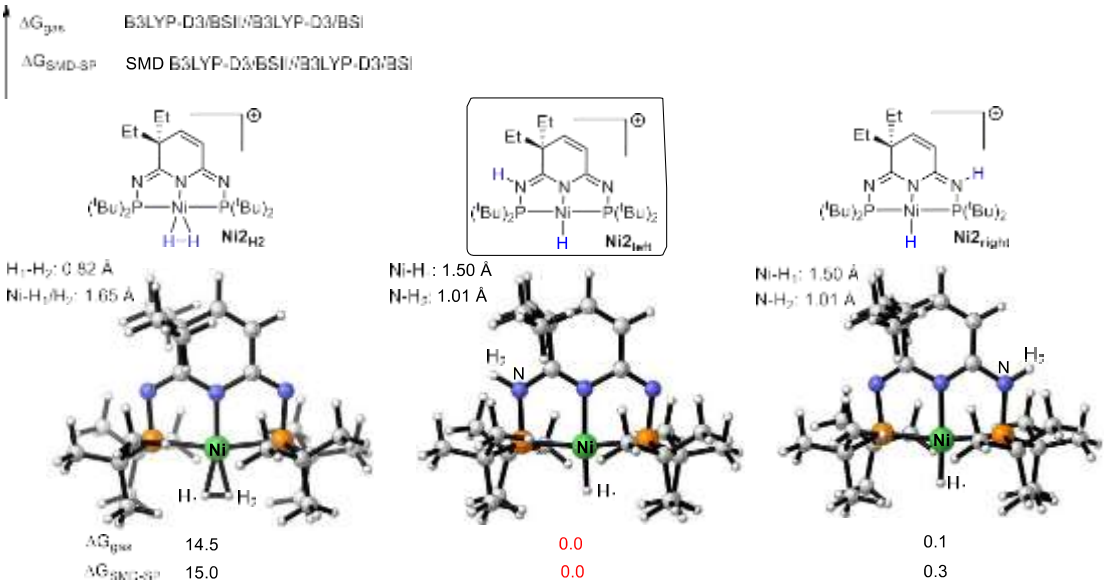

Fig. S21 The structures with relative Gibbs free energy data of the intermediates before and after H_2 splitting on the PN^3P-Ni species with two ethyl groups. (The energetics in the first and second line represent the energies in gas phase and the experimental solution (benzene) phase respectively.)

Ni2$_{left}$ in which the proton binds to the N atom on the left arm side is the most stable with respect to relative Gibbs free energy and set as the energy zero point. Its counterpart **Ni2$_{right}$** is only about 0.1-0.3 kcal/mol higher than **Ni2$_{left}$**, showing a very small selectivity. The initial **Ni2$_{H2}$** before H_2 splitting in which H_2 binds to the Ni center is 14.5-15.0 kcal/mol higher than **Ni2$_{left}$**, indicating the similar thermodynamic favorable property of the hydrogen cleavage in this Ni-Pincer complex.

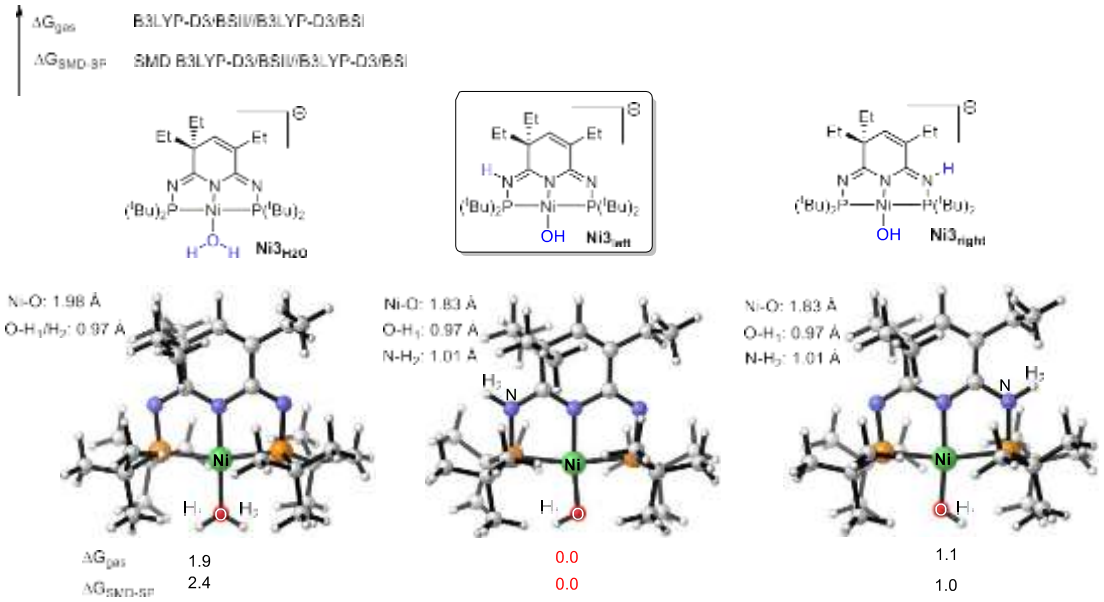

Fig. S22 The structures with relative Gibbs free energy data of the intermediates before and after H_2O splitting on the PN^3P-Ni species with three ethyl groups. (The energetics in the first and second line represent the energies in gas phase and the experimental solution (benzene) phase respectively.)

For the water splitting process, the Gibbs free energy for **Ni3$_{left}$** in which the proton binds to the N atom on the left arm side is the lowest and **Ni3$_{left}$** is set as the energy zero point. The counterpart **Ni3$_{right}$** with the proton connecting to the N atom on the right side is about 1.0-1.1 kcal/mol higher. The initial **Ni3$_{H2O}$** before H_2O splitting in which H_2O binds to the Ni center is 1.9-2.4 kcal/mol higher than **Ni3$_{left}$**. The splitting of H_2O is less favorable thermodynamically with respect to the Gibbs free energy variation of this process.

$Ni1_{H2}$

C	-1.176727	1.435966	-0.084899
C	-1.204441	2.961677	-0.085015
C	0.126384	3.556162	-0.419317
H	0.134079	4.635798	-0.563224
C	1.278959	2.875381	-0.487903
C	1.252438	1.417659	-0.274613
C	-1.601693	3.418442	1.363352
H	-1.687534	4.512010	1.348960
H	-2.603439	3.020296	1.559885
C	-0.632878	2.992526	2.470546
H	-0.519354	1.903687	2.514103
H	-1.003572	3.326115	3.444983
H	0.361820	3.425509	2.324307
C	-2.279994	3.477289	-1.083522
H	-3.253944	3.100640	-0.757899
H	-2.309879	4.570697	-0.994537
C	-2.025686	3.084842	-2.540821
H	-1.051353	3.442066	-2.892871
H	-2.794673	3.510544	-3.193075
H	-2.051206	1.996705	-2.667120
C	2.614951	3.544290	-0.718825
H	2.440259	4.510960	-1.204938
H	3.214815	2.938425	-1.405419
C	3.398976	3.762654	0.586921
H	2.835948	4.400224	1.278025
H	4.358651	4.248498	0.382430
H	3.598875	2.808985	1.084100
C	-3.057361	-1.500426	-1.462065
C	-3.389282	-2.997511	-1.345979
H	-4.188540	-3.189130	-0.624615
H	-2.515159	-3.598411	-1.065560
H	-3.734771	-3.361500	-2.320655
C	-4.325028	-0.684590	-1.783418
H	-4.728407	-1.027351	-2.743929
H	-4.104140	0.382726	-1.862937
H	-5.105231	-0.816774	-1.030019
C	-2.014403	-1.294067	-2.584413
H	-1.127908	-1.922245	-2.432644
H	-1.685823	-0.252133	-2.652209
H	-2.458055	-1.569930	-3.548202
C	-3.028170	-1.319308	1.726915
C	-2.343417	-0.427464	2.785006
H	-2.581741	0.628239	2.636849
H	-1.251977	-0.540979	2.764222
H	-2.692321	-0.722003	3.781530
C	-2.751998	-2.796153	2.068469
H	-3.207684	-3.025376	3.038785
H	-1.677681	-2.994981	2.160237
H	-3.172919	-3.491853	1.338770
C	-4.540528	-1.033331	1.703044
H	-4.943837	-1.160588	2.714931
H	-5.078933	-1.723961	1.047193
H	-4.749381	-0.008189	1.382358
C	2.980574	-1.646310	-1.623598
C	2.274955	-0.916637	-2.788268
H	2.542563	0.142624	-2.822055
H	1.183124	-0.993493	-2.711302
H	2.578549	-1.379020	-3.734631
C	4.500093	-1.416285	-1.703274
H	5.043968	-2.020030	-0.970514
H	4.756220	-0.363215	-1.552745
H	4.853465	-1.711865	-2.698505
C	2.649126	-3.149028	-1.700465
H	3.069862	-3.557826	-2.626455
H	1.567060	-3.322548	-1.731429
H	3.069279	-3.722497	-0.870050
C	3.125182	-1.270220	1.556076
C	4.473463	-0.529718	1.651170
H	4.883274	-0.676166	2.657835
H	4.354128	0.543348	1.482037
H	5.207542	-0.909954	0.937348
C	3.323275	-2.783774	1.742445
H	4.059582	-3.191330	1.043570
H	2.387313	-3.345068	1.628889
H	3.695302	-2.973218	2.756075
C	2.168163	-0.730976	2.644643
H	2.626180	-0.871386	3.630653
H	1.208732	-1.263425	2.642227
H	1.967332	0.337743	2.515757
N	0.028002	0.751537	-0.111718
N	-2.319444	0.824514	-0.001211
N	2.382079	0.772352	-0.261522
Ni	0.015597	-1.123708	0.057777
P	-2.212808	-0.860482	0.095440
P	2.241657	-0.900183	-0.062978
H	0.412230	-2.718228	0.213666
H	-0.404197	-2.712740	0.211141

$Ni1_{left}$

C	-1.050360	1.517372	-0.106304
C	-1.094208	3.033259	-0.129390
C	0.276495	3.592571	-0.394790
H	0.314308	4.674052	-0.516089

C	1.414527	2.882110	-0.433717
C	1.339149	1.421092	-0.255568
C	-1.571656	3.529105	1.281899
H	-1.637046	4.622424	1.230477
H	-2.595583	3.168754	1.447722
C	-0.672388	3.115088	2.450220
H	-0.571930	2.026616	2.522586
H	-1.093095	3.473998	3.394409
H	0.332400	3.535336	2.347534
C	-2.085621	3.544935	-1.218127
H	-3.112670	3.274658	-0.936620
H	-2.054674	4.640512	-1.187844
C	-1.779566	3.053612	-2.635170
H	-0.764846	3.330050	-2.939590
H	-2.479125	3.492201	-3.352928
H	-1.865916	1.963664	-2.710709
C	2.774883	3.514953	-0.602965
H	2.651400	4.503834	-1.059004
H	3.371982	2.907982	-1.291168
C	3.524514	3.652984	0.734282
H	2.965145	4.285759	1.432824
H	4.507074	4.108779	0.576026
H	3.673813	2.674044	1.198507
C	-3.144308	-1.461225	-1.431528
C	-3.569769	-2.934818	-1.288385
H	-4.370032	-3.065253	-0.554193
H	-2.728527	-3.579144	-1.010236
H	-3.951336	-3.286931	-2.253880
C	-4.365855	-0.571566	-1.727726
H	-4.860094	-0.941038	-2.633908
H	-4.075806	0.466468	-1.924215
H	-5.106961	-0.584832	-0.924487
C	-2.124705	-1.337844	-2.586360
H	-1.272310	-2.008701	-2.435782
H	-1.739609	-0.317110	-2.685782
H	-2.611973	-1.605135	-3.531562
C	-3.047273	-1.271879	1.746260
C	-2.299197	-0.410314	2.787285
H	-2.493879	0.657400	2.652022
H	-1.215794	-0.572994	2.742221
H	-2.639877	-0.687875	3.791273
C	-2.826076	-2.760869	2.090559
H	-3.209364	-2.949077	3.100296
H	-1.762007	-3.017386	2.073018
H	-3.352123	-3.434308	1.409993
C	-4.544422	-0.924037	1.758552
H	-4.936781	-1.062148	2.773070
H	-5.124501	-1.569685	1.093527
H	-4.732044	0.119977	1.479679
C	2.924321	-1.704788	-1.640807
C	2.191090	-0.967474	-2.784262
H	2.437173	0.098248	-2.804265
H	1.102468	-1.072140	-2.695518
H	2.493861	-1.404726	-3.742892
C	4.438130	-1.458794	-1.746787
H	4.999565	-2.070728	-1.034669
H	4.690388	-0.406763	-1.581941
H	4.776407	-1.735987	-2.752717
C	2.600569	-3.208684	-1.732614
H	2.941935	-3.585317	-2.704357
H	1.523976	-3.389482	-1.650724
H	3.103307	-3.793568	-0.958273
C	3.096557	-1.389619	1.537434
C	4.469994	-0.698632	1.618642
H	4.891739	-0.871477	2.616351
H	4.389268	0.380499	1.463847
H	5.178585	-1.095497	0.888706
C	3.239429	-2.912669	1.705212
H	3.966677	-3.333166	1.004190
H	2.282883	-3.429962	1.570926
H	3.600489	-3.127859	2.718063
C	2.177571	-0.834465	2.649932
H	2.644290	-1.010220	3.626471
H	1.200992	-1.332799	2.644321
H	2.018615	0.244697	2.544404
H	0.037299	-2.644340	0.202357
N	0.060230	0.811950	-0.128231
N	-2.216025	0.831978	-0.013206
N	2.407458	0.701274	-0.236730
Ni	-0.000672	-1.153221	0.050334
P	-2.184356	-0.935963	0.105888
P	2.174061	-1.011441	-0.059822
H	-3.077463	1.364099	0.000676

Ni1$_{\mathbf{right}}$

C	-1.259715	1.431848	-0.086000
C	-1.343843	2.954275	-0.104058
C	-0.025764	3.591772	-0.419850
H	-0.049751	4.671008	-0.565221
C	1.156004	2.951523	-0.475869
C	1.124199	1.500287	-0.262863
C	-1.775829	3.421698	1.331788
H	-1.911334	4.509958	1.303038
H	-2.760789	2.977747	1.514273
C	-0.809765	3.047190	2.459917

H	-0.652401	1.964729	2.516542
H	-1.213703	3.372540	3.423634
H	0.168172	3.523479	2.332163
C	-2.416875	3.423779	-1.127773
H	-3.376720	3.002805	-0.814521
H	-2.499065	4.515267	-1.048096
C	-2.118880	3.027290	-2.575837
H	-1.159180	3.431053	-2.919505
H	-2.898183	3.405717	-3.244452
H	-2.087360	1.938180	-2.688671
C	2.469717	3.673146	-0.689958
H	2.258982	4.639744	-1.158895
H	3.093882	3.129991	-1.413871
C	3.248654	3.909483	0.618697
H	2.664237	4.534388	1.301661
H	4.196970	4.417349	0.417965
H	3.471533	2.974122	1.145649
C	-3.016563	-1.606624	-1.442324
C	-3.306048	-3.112705	-1.315831
H	-4.098699	-3.318674	-0.590825
H	-2.412478	-3.678586	-1.029631
H	-3.645776	-3.491932	-2.287117
C	-4.308518	-0.824810	-1.744774
H	-4.723450	-1.185710	-2.693895
H	-4.117211	0.247336	-1.839248
H	-5.070659	-0.966865	-0.975335
C	-2.001469	-1.384106	-2.586068
H	-1.096148	-1.981949	-2.431941
H	-1.708592	-0.332027	-2.674085
H	-2.453714	-1.685947	-3.538382
C	-2.971965	-1.413877	1.735981
C	-2.295838	-0.505936	2.786513
H	-2.552546	0.545800	2.635171
H	-1.203195	-0.606496	2.760660
H	-2.636589	-0.798508	3.786584
C	-2.665752	-2.883707	2.084447
H	-3.059260	-3.098748	3.085259
H	-1.587644	-3.073465	2.089341
H	-3.131514	-3.587363	1.390606
C	-4.486884	-1.150985	1.722631
H	-4.882706	-1.282762	2.737136
H	-5.017862	-1.852618	1.072635
H	-4.716204	-0.130799	1.399342
C	3.024626	-1.597513	-1.628797
C	2.243690	-0.919539	-2.777355
H	2.430179	0.157983	-2.824520
H	1.163757	-1.077680	-2.678262
H	2.562593	-1.356786	-3.730388
C	4.523048	-1.279117	-1.750096
H	5.119670	-1.822408	-1.011968
H	4.733152	-0.207677	-1.646688
H	4.875364	-1.582731	-2.743023
C	2.782106	-3.120691	-1.699798
H	3.130796	-3.488338	-2.672004
H	1.717684	-3.357094	-1.603240
H	3.326136	-3.669722	-0.927133
C	3.209119	-1.221952	1.538301
C	4.498798	-0.385002	1.614391
H	4.988452	-0.579700	2.575868
H	4.292500	0.690389	1.576446
H	5.215153	-0.633067	0.827988
C	3.528308	-2.721264	1.691398
H	4.292837	-3.052497	0.982177
H	2.636696	-3.345121	1.564075
H	3.918559	-2.899756	2.700136
C	2.244906	-0.781195	2.663667
H	2.742194	-0.900367	3.633598
H	1.333351	-1.388756	2.667874
H	1.955257	0.271091	2.563244
H	-0.011085	-2.651059	0.194319
N	-0.000896	0.807249	-0.099888
N	-2.342634	0.742789	-0.001615
N	2.278181	0.788827	-0.240361
Ni	0.037999	-1.156348	0.073658
P	-2.139251	-0.980115	0.105097
P	2.218867	-0.970386	-0.045431
H	3.148152	1.288131	-0.373682

$Ni1_{mid}$

C	-1.265463	1.468743	0.020663
C	-1.285399	2.982159	-0.074297
C	0.056750	3.529480	-0.485621
H	0.043878	4.587218	-0.745281
C	1.229857	2.872352	-0.560910
C	1.284941	1.450476	-0.218387
C	-1.654768	3.558225	1.341083
H	-1.657201	4.650576	1.244064
H	-2.686177	3.255574	1.555917
C	-0.736541	3.157075	2.500064
H	-0.852584	2.100851	2.773707
H	-0.984952	3.735322	3.395007
H	0.317622	3.347047	2.267676
C	-2.368971	3.450530	-1.087811
H	-3.336843	3.070134	-0.748073

H	-2.416720	4.545153	-1.030492
C	-2.115971	3.020676	-2.535056
H	-1.160345	3.401789	-2.912064
H	-2.907333	3.401750	-3.187758
H	-2.106317	1.929975	-2.630592
C	2.521632	3.542668	-0.972255
H	2.285189	4.481591	-1.484636
H	3.043957	2.902273	-1.691165
C	3.445748	3.823410	0.225133
H	2.958603	4.486114	0.949279
H	4.368646	4.307183	-0.109588
H	3.717875	2.894281	0.735201
C	-2.990337	-1.575710	-1.502031
C	-3.312510	-3.076435	-1.379341
H	-4.134254	-3.265286	-0.682574
H	-2.440139	-3.659088	-1.062578
H	-3.624470	-3.451478	-2.361161
C	-4.255113	-0.769605	-1.850131
H	-4.640947	-1.125887	-2.812864
H	-4.041959	0.298509	-1.942737
H	-5.048014	-0.895608	-1.109838
C	-1.929349	-1.379306	-2.607906
H	-1.041139	-1.989344	-2.413547
H	-1.617730	-0.332504	-2.698107
H	-2.351072	-1.683486	-3.573118
C	-3.071119	-1.360971	1.674592
C	-2.426870	-0.452514	2.744432
H	-2.646559	0.604470	2.566603
H	-1.338123	-0.591612	2.786427
H	-2.828455	-0.715548	3.729592
C	-2.794734	-2.831811	2.049157
H	-3.223674	-3.032130	3.038194
H	-1.719598	-3.036351	2.091858
H	-3.246714	-3.535525	1.346467
C	-4.580026	-1.079510	1.597515
H	-5.019070	-1.200798	2.595261
H	-5.091673	-1.778701	0.930315
H	-4.785625	-0.059040	1.259296
C	2.998938	-1.708038	-1.568715
C	2.220187	-1.078757	-2.746032
H	2.417990	-0.006681	-2.837166
H	1.139208	-1.226797	-2.637984
H	2.533213	-1.562709	-3.678449
C	4.495853	-1.386375	-1.702513
H	5.096076	-1.931480	-0.968251
H	4.693156	-0.315319	-1.595427
H	4.838823	-1.695870	-2.697115
C	2.758634	-3.230625	-1.568418
H	3.122249	-3.644231	-2.516520
H	1.693959	-3.467439	-1.476625
H	3.293258	-3.739984	-0.762145
C	3.194113	-1.161495	1.574653
C	4.535804	-0.407448	1.568001
H	4.975799	-0.461446	2.571302
H	4.407525	0.647737	1.310150
H	5.253522	-0.842993	0.870883
C	3.406740	-2.658899	1.863387
H	4.124653	-3.106967	1.170297
H	2.469815	-3.225017	1.810069
H	3.813549	-2.775120	2.874976
C	2.280053	-0.554947	2.664643
H	2.755690	-0.670930	3.645347
H	1.305602	-1.058041	2.702200
H	2.124562	0.520384	2.508697
H	-0.002148	-2.651816	0.028160
N	0.043414	0.836059	0.336181
N	-2.312675	0.762097	-0.068645
N	2.337564	0.740933	-0.343715
Ni	0.026653	-1.182809	0.151339
P	-2.148072	-0.985317	0.076518
P	2.210554	-0.978161	-0.025573
H	0.141302	0.904393	1.357108

$Ni2_{H2}$

C	-1.373147	1.351193	-0.085725
C	-1.780114	2.826722	-0.083682
C	-0.636135	3.736478	-0.410554
H	-0.883268	4.787239	-0.547566
C	0.632734	3.325287	-0.488379
C	0.983312	1.922388	-0.282738
C	-2.288418	3.167166	1.361035
H	-2.640546	4.206109	1.348216
H	-3.163094	2.534224	1.547160
C	-1.253981	2.986578	2.475961
H	-0.881787	1.957132	2.521405
H	-1.702089	3.219728	3.447013
H	-0.392200	3.647265	2.337803
C	-2.942209	3.061358	-1.091221
H	-3.793357	2.453244	-0.771628
H	-3.244393	4.112570	-1.001848
C	-2.589481	2.746606	-2.546968
H	-1.734136	3.336404	-2.895267
H	-3.437467	2.966973	-3.202891
H	-2.341473	1.686845	-2.673044

C	-2.461259	-1.949535	-1.477488
C	-2.420400	-3.482954	-1.367876
H	-3.155493	-3.866268	-0.654688
H	-1.428985	-3.854656	-1.080549
H	-2.658544	-3.915349	-2.346711
C	-3.886578	-1.464883	-1.808137
H	-4.186921	-1.891788	-2.772655
H	-3.931275	-0.375602	-1.884032
H	-4.617292	-1.785494	-1.061774
C	-1.490563	-1.491075	-2.589954
H	-0.479699	-1.886908	-2.432229
H	-1.422904	-0.400275	-2.651664
H	-1.846734	-1.861103	-3.558453
C	-2.499622	-1.783297	1.712734
C	-2.058608	-0.758536	2.780072
H	-2.544468	0.208938	2.634235
H	-0.971941	-0.604800	2.768670
H	-2.333369	-1.134616	3.772340
C	-1.875691	-3.151133	2.049611
H	-2.268364	-3.490032	3.015336
H	-0.785904	-3.084137	2.148942
H	-2.110644	-3.923400	1.313490
C	-4.036052	-1.872371	1.678288
H	-4.402847	-2.099722	2.686505
H	-4.386804	-2.669031	1.015571
H	-4.485230	-0.926552	1.360483
C	3.429261	-0.620626	-1.606772
C	2.575790	-0.094456	-2.782034
H	2.576903	0.997739	-2.824664
H	1.535380	-0.435723	-2.710082
H	2.990202	-0.476514	-3.722183
C	4.848754	-0.030751	-1.681245
H	5.515197	-0.473562	-0.934923
H	4.841668	1.055149	-1.547862
H	5.272728	-0.247533	-2.669157
C	3.471542	-2.159603	-1.669340
H	3.985345	-2.462676	-2.588969
H	2.463482	-2.589118	-1.704150
H	4.011444	-2.607406	-0.830948
C	3.462728	-0.188574	1.567954
C	4.565066	0.884289	1.665840
H	5.000139	0.848085	2.671935
H	4.162973	1.886957	1.500015
H	5.372979	0.715291	0.950286
C	4.053664	-1.595598	1.757230
H	4.873715	-1.795041	1.061332
H	3.299774	-2.384588	1.642523
H	4.459208	-1.678482	2.772318
C	2.392156	0.076747	2.651948
H	2.867481	0.066940	3.639707
H	1.610993	-0.693961	2.648616
H	1.912223	1.052047	2.519300
N	-0.036892	0.977804	-0.113741
N	-2.329870	0.478115	-0.001806
N	2.241342	1.593037	-0.271866
Ni	0.417097	-0.836913	0.064675
P	-1.809879	-1.130625	0.089404
P	2.521637	-0.063784	-0.056355
H	1.460508	3.996084	-0.687474
H	1.198309	-2.282088	0.236230
H	0.406959	-2.480058	0.229884

$Ni2_{left}$

C	-1.288207	1.438708	-0.067243
C	-1.735368	2.892444	-0.053772
C	-0.559446	3.805200	-0.283912
H	-0.798475	4.862664	-0.373281
C	0.710649	3.389178	-0.340283
C	1.041443	1.972476	-0.202858
C	-2.343919	3.206331	1.358131
H	-2.694338	4.245046	1.331832
H	-3.239299	2.585649	1.493933
C	-1.383459	3.008852	2.534297
H	-1.005500	1.981886	2.584709
H	-1.895496	3.221646	3.477545
H	-0.520941	3.677854	2.461451
C	-2.813040	3.152406	-1.150315
H	-3.733498	2.610849	-0.893192
H	-3.075882	4.215442	-1.094258
C	-2.371697	2.797758	-2.572493
H	-1.465504	3.343100	-2.855545
H	-3.156443	3.051555	-3.291233
H	-2.162558	1.726782	-2.673473
C	-2.503664	-1.943660	-1.499779
C	-2.528889	-3.480936	-1.405078
H	-3.276183	-3.839641	-0.691471
H	-1.551630	-3.890762	-1.127299
H	-2.792135	-3.890150	-2.387417
C	-3.912199	-1.396336	-1.795711
H	-4.281452	-1.854034	-2.720958

H	-3.902265	-0.312974	-1.958425	N	-2.231597	0.468469	-0.001293
H	-4.633349	-1.628157	-1.007824	N	2.265739	1.573993	-0.190414
C	-1.538749	-1.521794	-2.630960	Ni	0.432452	-0.863527	0.043054
H	-0.542486	-1.951750	-2.483062	P	-1.732618	-1.232917	0.069694
H	-1.432082	-0.433376	-2.694503	P	2.494888	-0.145790	-0.038082
H	-1.928668	-1.876447	-3.592424	H	-3.203458	0.752258	0.017998
C	-2.494051	-1.834600	1.684068	H	1.542703	4.070092	-0.479501
C	-2.006094	-0.842326	2.762502				
H	-2.470286	0.142049	2.653860				
H	-0.917159	-0.717193	2.733161				
H	-2.273641	-1.230670	3.751782				
C	-1.895616	-3.225100	1.989042				
H	-2.225093	-3.538540	2.986582				
H	-0.801346	-3.195400	1.981842				
H	-2.222445	-3.990218	1.281119				
C	-4.030152	-1.888447	1.679800				
H	-4.382690	-2.154316	2.683423				
H	-4.416144	-2.642330	0.988266				
H	-4.480437	-0.921112	1.425863				
C	3.417657	-0.594118	-1.615991				
C	2.534632	-0.050550	-2.761931				
H	2.498824	1.042755	-2.764362				
H	1.508565	-0.433322	-2.692839				
H	2.951993	-0.379571	-3.720776				
C	4.819322	0.032747	-1.692092				
H	5.506376	-0.421006	-0.971691				
H	4.791062	1.112849	-1.519030				
H	5.234508	-0.140247	-2.692517				
C	3.491706	-2.129120	-1.732884				
H	3.933497	-2.388460	-2.702531				
H	2.496148	-2.580605	-1.674638				
H	4.114928	-2.579645	-0.956391				
C	3.470242	-0.290032	1.566564				
C	4.586599	0.763956	1.684849				
H	5.038269	0.685736	2.681406				
H	4.197747	1.778361	1.562848				
H	5.380696	0.612084	0.950664				
C	4.041361	-1.712591	1.701075				
H	4.863225	-1.889904	1.001002				
H	3.273632	-2.478238	1.542657				
H	4.441813	-1.841399	2.713778				
C	2.420866	-0.051947	2.676665				
H	2.910324	-0.110692	3.656120				
H	1.629437	-0.810014	2.644668				
H	1.958697	0.938271	2.593109				
H	0.866222	-2.293301	0.171772				
N	-0.031294	1.046811	-0.097233				

Ni2$_{right}$

C	-1.457754	1.341331	-0.078453
C	-1.907752	2.802683	-0.081748
C	-0.781621	3.746570	-0.382419
H	-1.052972	4.792155	-0.512658
C	0.505754	3.375138	-0.449124
C	0.837744	1.972949	-0.255753
C	-2.450050	3.136300	1.353389
H	-2.845246	4.159477	1.333490
H	-3.299389	2.464769	1.520642
C	-1.430626	2.992988	2.487549
H	-1.017871	1.979544	2.536025
H	-1.909022	3.200189	3.449777
H	-0.595823	3.692817	2.375012
C	-3.055051	3.010047	-1.112552
H	-3.884920	2.364423	-0.810668
H	-3.401137	4.047590	-1.022914
C	-2.661341	2.713534	-2.561724
H	-1.830467	3.345349	-2.897104
H	-3.507621	2.893847	-3.231609
H	-2.361163	1.667151	-2.683463
C	-2.424416	-2.015827	-1.470010
C	-2.343306	-3.548597	-1.358777
H	-3.064515	-3.946527	-0.639121
H	-1.340361	-3.885734	-1.074184
H	-2.579939	-3.988383	-2.335070
C	-3.865754	-1.564731	-1.771436
H	-4.178979	-2.004718	-2.726157
H	-3.938186	-0.477106	-1.854623
H	-4.573312	-1.894434	-1.007468
C	-1.489759	-1.544016	-2.606668
H	-0.467223	-1.906990	-2.453419
H	-1.459314	-0.451585	-2.684535
H	-1.853264	-1.937118	-3.563650
C	-2.434335	-1.852876	1.710829
C	-2.000097	-0.820044	2.773727
H	-2.504075	0.139674	2.632550
H	-0.915662	-0.652489	2.752028
H	-2.261603	-1.197806	3.769068
C	-1.782359	-3.208875	2.045267
H	-2.113546	-3.523488	3.042261
H	-0.690373	-3.132504	2.052338
H	-2.063414	-3.996565	1.342415
C	-3.967882	-1.963550	1.693090
H	-4.321861	-2.198306	2.704432
H	-4.312666	-2.765368	1.033682
H	-4.436251	-1.025339	1.379640
C	3.457911	-0.559351	-1.610194
C	2.548355	-0.093475	-2.769603
H	2.465354	0.996792	-2.818124
H	1.539291	-0.512365	-2.682396
H	2.976087	-0.439347	-3.717517
C	4.836111	0.112287	-1.716317
H	5.536137	-0.265358	-0.965736
H	4.779048	1.203251	-1.620831
H	5.265321	-0.103425	-2.701916
C	3.592633	-2.096189	-1.677282
H	4.029039	-2.369096	-2.645255
H	2.616523	-2.583722	-1.589442
H	4.246630	-2.495999	-0.898370
C	3.509791	-0.150064	1.557650
C	4.544830	0.985881	1.650488
H	5.059282	0.915025	2.616089
H	4.072310	1.973756	1.614822
H	5.307886	0.931824	0.870456
C	4.195616	-1.520962	1.710671
H	5.026706	-1.645046	1.009986
H	3.492077	-2.349320	1.572043
H	4.607247	-1.599936	2.723597
C	2.453362	0.025654	2.672805
H	2.954780	0.034417	3.647844
H	1.727757	-0.795052	2.666835
H	1.904998	0.969080	2.570317
H	0.746741	-2.323982	0.175123
N	-0.085314	1.030242	-0.096498
N	-2.342562	0.411894	-0.001677
N	2.133216	1.578218	-0.236355
Ni	0.430774	-0.860512	0.064769
P	-1.727311	-1.213841	0.088134
P	2.507001	-0.145176	-0.038081
H	2.847009	2.287275	-0.361405
H	1.305540	4.084990	-0.635897

$Ni3_{H2O}$

C	-1.171288	1.520597	-0.089451
C	-1.196349	3.047754	-0.085917
C	0.137783	3.642444	-0.403097
H	0.149861	4.723116	-0.539398
C	1.287364	2.957371	-0.466573
C	1.255573	1.496718	-0.265367
C	-1.610630	3.502167	1.357626
H	-1.692584	4.596177	1.346019
H	-2.616068	3.106923	1.540606
C	-0.657086	3.069460	2.475327
H	-0.547836	1.980140	2.515266
H	-1.037986	3.400769	3.446710
H	0.340894	3.499126	2.341984
C	-2.258921	3.567943	-1.095893
H	-3.237048	3.190592	-0.784196
H	-2.289020	4.661218	-1.003795
C	-1.986468	3.180232	-2.551134
H	-1.007790	3.538624	-2.889704
H	-2.747432	3.607522	-3.211842
H	-2.009810	2.092498	-2.680403
C	2.627179	3.624110	-0.681208
H	2.459465	4.595350	-1.160834
H	3.231442	3.021834	-1.366880
C	3.400471	3.829979	0.632919
H	2.833529	4.464465	1.323763
H	4.364010	4.313636	0.441198
H	3.591570	2.871580	1.124472
C	-3.072315	-1.403638	-1.475967
C	-3.389155	-2.904977	-1.361513
H	-4.171249	-3.110086	-0.624557
H	-2.498881	-3.493988	-1.109305
H	-3.752921	-3.268156	-2.330008
C	-4.344085	-0.597770	-1.800951
H	-4.731711	-0.926805	-2.772937
H	-4.132601	0.473036	-1.859217
H	-5.133656	-0.750179	-1.061503
C	-2.030651	-1.193545	-2.599374
H	-1.139303	-1.812416	-2.442198
H	-1.712717	-0.148513	-2.670518
H	-2.472090	-1.476210	-3.562430
C	-3.076817	-1.209832	1.700663
C	-2.443356	-0.288406	2.764462
H	-2.707682	0.757753	2.595995
H	-1.348719	-0.369297	2.766845
H	-2.805609	-0.579953	3.757527
C	-2.766990	-2.672517	2.079474
H	-3.297157	-2.930060	3.003769
H	-1.696748	-2.802624	2.297420
H	-3.080269	-3.394197	1.319012
C	-4.595444	-0.971846	1.645219
H	-5.016412	-1.089218	2.651454
H	-5.102422	-1.688167	0.992080
H	-4.825134	0.040563	1.299751
C	3.022485	-1.547032	-1.626735
C	2.332602	-0.806865	-2.794331
H	2.606089	0.251123	-2.816193
H	1.239580	-0.878370	-2.727782
H	2.643205	-1.263433	-3.741513
C	4.542638	-1.328947	-1.692795
H	5.076862	-1.947269	-0.964839
H	4.805002	-0.280375	-1.523154
H	4.903413	-1.611440	-2.689452
C	2.677902	-3.046707	-1.724021
H	3.117657	-3.458125	-2.640092
H	1.595050	-3.204205	-1.788995
H	3.079156	-3.631168	-0.889215
C	3.144598	-1.179075	1.546616
C	4.508583	-0.468389	1.631035
H	4.905771	-0.581560	2.647302
H	4.413589	0.599246	1.417316
H	5.241554	-0.892020	0.941203
C	3.313444	-2.693234	1.757166
H	4.007322	-3.139330	1.038843
H	2.354946	-3.228666	1.699488
H	3.715575	-2.878802	2.760080
C	2.206167	-0.608638	2.635346
H	2.658498	-0.759846	3.622618
H	1.228034	-1.106526	2.631185
H	2.039680	0.465035	2.501487
N	0.030859	0.831597	-0.108263
N	-2.322183	0.920237	-0.016313
N	2.389863	0.857032	-0.257952
Ni	0.012607	-1.066028	0.044080
P	-2.218948	-0.766197	0.080635
P	2.246897	-0.818832	-0.072389
O	-0.058263	-3.047221	0.128847
H	0.781506	-3.507401	0.293473
H	-0.711711	-3.406141	0.753945

$Ni3_{left}$

C	-1.039973	1.585224	-0.066212
C	-1.067742	3.101142	-0.003092
C	0.280141	3.666967	-0.347352
H	0.316700	4.751397	-0.436618
C	1.405414	2.950521	-0.484192
C	1.336447	1.487238	-0.326003
C	-1.423053	3.509256	1.473341
H	-1.466981	4.604562	1.496505
H	-2.439244	3.156077	1.693235
C	-0.448347	3.003475	2.540308
H	-0.380089	1.910385	2.548374
H	-0.780668	3.323032	3.532599
H	0.559118	3.398342	2.379401
C	-2.138565	3.689968	-0.970189
H	-3.144686	3.415469	-0.623977
H	-2.089047	4.780637	-0.870504
C	-1.955767	3.292483	-2.436970
H	-0.965178	3.579740	-2.804237
H	-2.704611	3.784708	-3.064513
H	-2.063162	2.211022	-2.577882
C	2.756880	3.578829	-0.729653
H	2.606832	4.584636	-1.138245
H	3.294356	2.995647	-1.484557
C	3.609829	3.663169	0.549151
H	3.103708	4.256901	1.318995
H	4.571903	4.138661	0.333248
H	3.805746	2.665274	0.951242
C	-3.273073	-1.245927	-1.466552
C	-3.726017	-2.716910	-1.399605
H	-4.487696	-2.883475	-0.632970
H	-2.889660	-3.400714	-1.213577
H	-4.164038	-2.996125	-2.364807
C	-4.488480	-0.317812	-1.648796
H	-5.031534	-0.619115	-2.552278
H	-4.186684	0.725377	-1.793852
H	-5.191277	-0.369065	-0.813243
C	-2.301118	-1.066466	-2.654514
H	-1.454570	-1.757581	-2.586958
H	-1.898548	-0.049149	-2.705594
H	-2.833169	-1.263182	-3.592704
C	-3.023998	-1.270917	1.710486
C	-2.205610	-0.496624	2.766671
H	-2.366825	0.583582	2.703090
H	-1.132484	-0.696159	2.667013
H	-2.515903	-0.823351	3.765589
C	-2.797927	-2.783995	1.929358
H	-3.080940	-3.037306	2.957629
H	-1.744984	-3.050843	1.785323
H	-3.410761	-3.398435	1.264604
C	-4.511382	-0.905136	1.826170
H	-4.854371	-1.115993	2.846051
H	-5.136005	-1.489687	1.144996
H	-4.693383	0.159975	1.637300
C	3.014086	-1.672831	-1.628141
C	2.023864	-1.380139	-2.778261
H	1.863400	-0.304578	-2.915419
H	1.055481	-1.858915	-2.597833
H	2.433129	-1.779154	-3.713923
C	4.377577	-1.036509	-1.953238
H	5.129447	-1.254307	-1.191639
H	4.302585	0.049272	-2.061526
H	4.739157	-1.452118	-2.901819
C	3.134219	-3.195634	-1.431756
H	3.394283	-3.657088	-2.392202
H	2.191520	-3.625740	-1.078280
H	3.928464	-3.449556	-0.723208
C	3.050120	-1.231337	1.546101
C	4.558108	-0.934660	1.514429
H	4.952708	-0.987070	2.536689
H	4.771778	0.063452	1.118766
H	5.102158	-1.672151	0.917670
C	2.773993	-2.686062	1.977768
H	3.324192	-3.406450	1.367983
H	1.710791	-2.933247	1.909898
H	3.106174	-2.811093	3.015699
C	2.348279	-0.274372	2.535965
H	2.723922	-0.470925	3.546690
H	1.263447	-0.435924	2.543889
H	2.542101	0.777059	2.302486
N	0.059954	0.864912	-0.157421
N	-2.216784	0.923386	0.038516
N	2.410721	0.781733	-0.350159
Ni	0.003949	-1.113444	-0.029313
P	-2.238028	-0.833986	0.056571
P	2.207963	-0.916064	-0.109066
H	-3.063042	1.475992	0.100241
O	0.125471	-2.928175	0.157164
H	-0.671596	-3.357988	-0.189847
Ni3$_{right}$			
C	-1.257783	1.512389	-0.081540

C	-1.323688	3.035842	-0.092761	H	-3.058605	-2.970696	3.101028
C	-0.010505	3.659967	-0.439290	H	-1.719943	-3.059246	1.920293
H	-0.025907	4.737791	-0.594973	H	-3.370842	-3.445223	1.429928
C	1.161297	3.004817	-0.508894	C	-4.510712	-0.958631	1.745448
C	1.122123	1.556841	-0.275241	H	-4.902340	-1.094840	2.761140
C	-1.714195	3.500686	1.356864	H	-5.078742	-1.621319	1.086047
H	-1.838411	4.590401	1.335524	H	-4.695838	0.077921	1.446038
H	-2.699470	3.066952	1.561053	C	3.024510	-1.549928	-1.625317
C	-0.725480	3.111115	2.460087	C	2.214959	-0.893748	-2.766964
H	-0.580306	2.026665	2.511749	H	2.401622	0.182401	-2.841801
H	-1.102048	3.439783	3.433665	H	1.138163	-1.050862	-2.638432
H	0.254931	3.575707	2.309847	H	2.510409	-1.351654	-3.717729
C	-2.417559	3.521371	-1.086845	C	4.520406	-1.244227	-1.791600
H	-3.374674	3.112799	-0.750661	H	5.132024	-1.772436	-1.054576
H	-2.482024	4.613602	-1.001415	H	4.739563	-0.171689	-1.721135
C	-2.161831	3.125433	-2.543147	H	4.845978	-1.576319	-2.784552
H	-1.205264	3.516319	-2.910006	C	2.761588	-3.072320	-1.649758
H	-2.952019	3.518177	-3.190331	H	3.053000	-3.464488	-2.631078
H	-2.150032	2.036445	-2.660300	H	1.700263	-3.292089	-1.490875
C	2.477786	3.713011	-0.754117	H	3.348995	-3.609032	-0.899263
H	2.265073	4.670628	-1.240082	C	3.271123	-1.102626	1.532587
H	3.089755	3.153988	-1.476347	C	4.571380	-0.279090	1.559162
C	3.274442	3.974100	0.539190	H	5.073569	-0.442581	2.520037
H	2.702222	4.618447	1.214309	H	4.377327	0.796634	1.483677
H	4.223174	4.471278	0.315161	H	5.271917	-0.565134	0.771449
H	3.498150	3.050269	1.085815	C	3.580541	-2.599502	1.724732
C	-3.037871	-1.512641	-1.446426	H	4.311646	-2.966428	0.998664
C	-3.315492	-3.019946	-1.295731	H	2.679518	-3.220423	1.657099
H	-4.132365	-3.214228	-0.594637	H	4.004702	-2.750363	2.724103
H	-2.422259	-3.559344	-0.964953	C	2.331221	-0.619048	2.660964
H	-3.620250	-3.420299	-2.270386	H	2.840463	-0.723515	3.626218
C	-4.327047	-0.734377	-1.766152	H	1.407793	-1.207621	2.693981
H	-4.741997	-1.116987	-2.706745	H	2.057796	0.435266	2.539762
H	-4.134951	0.335572	-1.886449	N	-0.002372	0.864006	-0.088923
H	-5.089795	-0.857734	-0.993649	N	-2.353562	0.848309	-0.005045
C	-2.008719	-1.305868	-2.580847	N	2.282135	0.856679	-0.257897
H	-1.122453	-1.927672	-2.418437	Ni	0.012633	-1.111029	0.072645
H	-1.692938	-0.259460	-2.665397	P	-2.185420	-0.867812	0.103124
H	-2.462645	-1.594854	-3.536302	P	2.256147	-0.886038	-0.040285
C	-3.010545	-1.296635	1.738679	H	3.143872	1.364549	-0.410498
C	-2.275947	-0.434351	2.788703	O	-0.163117	-2.932324	0.073169
H	-2.469481	0.632267	2.645321	H	0.615371	-3.354063	0.468067
H	-1.191770	-0.601634	2.756832				
H	-2.629771	-0.710219	3.788788				
C	-2.769543	-2.785838	2.059293				

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